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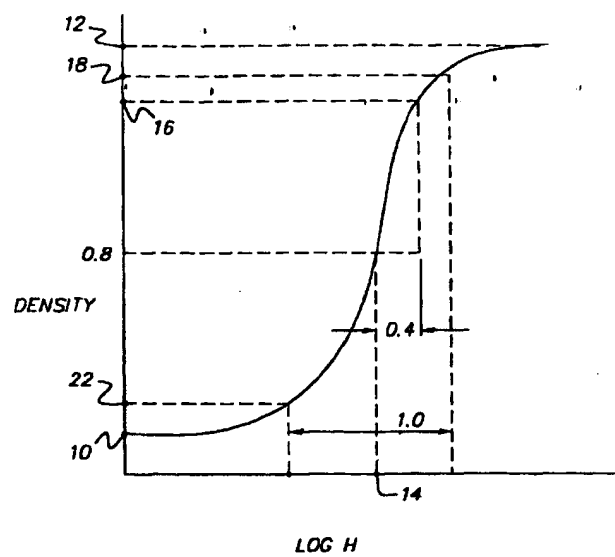
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(54) **Color paper with exceptional reciprocity performance**

(57) The invention relates to a negative working reflective base photographic element comprising support material wherein said support material comprises a paper base and overlaying said paper base are full color photographic silver halide containing imaging layers wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 10 percent as a function of the red shoulder color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 8 percent as a function of the green shoulder color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 5 percent as a function of the blue shoulder color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 6 percent as a function of the red Dmax color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 9 percent as a function of the green Dmax color record, wherein said photo-

graphic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 5 percent as a function of the blue Dmax color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 9 percent as a function of the red inmax color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 10 percent as a function of the green inmax color record, and wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 5 percent as a function of the blue inmax color record.

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Description

FIELD OF THE INVENTION

- 5 [0001] This invention relates to photographic materials. It particularly relates to color photographic papers utilizing reflective base materials.

BACKGROUND OF THE INVENTION

- 10 [0002] The continuing thrust towards digital printing of photographic color papers has created the need for a consumer color paper that can work in both a negative working optical and digital exposure equipment. In order for a color paper to correctly print, utilizing a color negative curve shape of the paper is critical. In a digital environment (direct writing) to a photographic paper, the curve shape to a degree can be electromodulated and thus have a greater degree of freedom than the color negative working system. Ideally, a color paper that could substantially maintain tone scale from conventional optical negative working exposure times to sub microsecond digital direct writing exposure times would be preferred. This would enable a photofinishing area to maintain one paper for both digital and optical exposure thereby reducing the need for expensive inventory.

- 15 [0003] It has been proposed in U.S. 5,744,287 to utilize emulsions in one or more color records having a shoulder contrast, significantly reduced high intensity reciprocity failure and narrower dynamic exposure ranges of less than 50 microseconds exposures for a digital color photographic paper. While the emulsion set described in U.S. 5,744,287 performs acceptably in direct writing sub microsecond exposure digital devices, the characteristic curve shape would not necessarily be optimized in a chemical negative working optical exposure system.

- 20 [0004] Of the artifacts associated with printing digital images onto silver halide media, formation of visually soft or "bleeding" edges, especially around text, probably elicits the greatest objections. In the current invention this artifact is designated "digital fringing", and it pertains to unwanted density formed in an area of a digital print as a result of a scanning exposure in a different area of the print, not necessarily in adjacent pixels. Digital fringing may be detected in pixels many lines away from area(s) of higher exposure, creating an underlying minimum density or D_{min} that reduces sharpness and degrades color reproduction. It should not be confused with system flare arising from improper calibration, which produces a similar macroscopic defect.

- 25 [0005] Digital fringing may be observed even with exposures producing mid scale densities. The minimum exposure at which digital fringing becomes visually objectionable varies by digital printing device and emulsion photographic properties. Because fringing increases with exposure, the useful density range for typical commercial color photographic papers printed by scanning laser or LED (light emitting diode) exposures must be restricted to 2.2 or below, less than the full density range of the papers. Fine line images require even lower print densities due to the acute sensitivity of the eye to softening of high contrast edges.

- 30 [0006] Other image artifacts associated with optical scan printing on silver halide media that should not be confused with digital fringing are "contouring", "banding", and "rastering". "Contouring" refers to the formation of discrete density steps in highlight regions where the gradations should appear continuous. Bit limited system modulators (those that use $\leq 2^{10}$ bits, or 1024 DAC levels, designated 10 bit), may have too few levels to calibrate for density differences that are below the detection threshold of the human eye. A single bit change in exposure may, therefore, produce a density change large enough to see as a step, or contour. Lower contrast toe regions of the paper H&D curves can alleviate contouring in a 10 bit system, as taught by Kawai, Kokai JP 05/142712-A, but the low contrast also lowers the density threshold for digital fringing. System modulators using 2^{12} bits (designated 12 bit, having 4096 DAC levels) are not as susceptible to contouring artifacts. "Banding" is the appearance of lines, or bands, having a lower frequency than the individual raster lines, but which are parallel to the line scan direction. The bands arise from non-uniformity in the overlap exposure between scans (e.g., from mechanical vibrations) causing fluctuations in exposure in the overlap areas large enough to produce a visually detectable difference in density. "Rastering" is a high frequency artifact related to non-optimal spot size or shape which allows the eye to resolve the individual scan lines.

- 35 [0007] Those skilled in the art will recognize that the optical properties of the media (the scattering of light by the emulsion layers and paper base) contribute in part to digital fringing, which is a loss of acutance or sharpness. A general discussion of acutance as it pertains to structure of photographic media can be found in Mees & James, *Theory of the Photographic Process, 4th Edition*, Chapter 21. The spot shape and spot size used in scanning laser exposures also contribute to loss of sharpness.

- 40 [0008] Typical chemical negative working color papers are restricted with regards to tone scale or contrast levels due to the fact that the paper must print acceptably with a color negative. Digital only color papers, however are not restricted as the digital printing device can electromodulate the curve shape to provide an acceptable tone scale in the image. It would be desirable to have a color paper that would provide not only excellent tone scale to optimize image quality in a negative working system, but also provide sufficient reciprocity control to survive the extremely short expo-

sure times typical in sub microsecond digital exposure devices.

PROBLEM TO BE SOLVED BY THE INVENTION

- 5 [0009] There is a need for color photographic materials on reflective base that provide improved imaging over a wide range of exposure times and with improved performance for digital imaging.

SUMMARY OF THE INVENTION

- 10 [0010] It is an object of the invention to overcome disadvantages of prior photographic products.
 [0011] It is another object to provide color photographic materials that may be imaged over a wide range of exposure times with exceptional images being formed.
 [0012] It is a further object to provide color paper materials that can be used in both digital and negative working optical printing systems.
- 15 [0013] These and other objects of the invention are accomplished by a negative working reflective base photographic element comprising support material wherein said support material comprises a paper base and overlaying said paper base are fill color photographic silver halide containing imaging layers wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 10 percent as a function of the red shoulder color record, wherein said photographic element has an exposure range of
- 20 between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 8 percent as a function of the green shoulder color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 5 percent as a function of the blue shoulder color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 6 percent as a function of the red Dmax color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 9 percent as a function of the green Dmax color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 5 percent as a function of the blue Dmax color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 9 percent as a function of the red inmax color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 10 percent as a function of the green inmax color record, and wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 5 percent as a function of the blue inmax color record.

35 ADVANTAGEOUS EFFECT OF THE INVENTION

- [0014] This invention provides a reflective photographic paper material that may be exposed over a wide range of exposure times and still provide exceptional image quality, with clear, sharp, and bright images.

40 BRIEF DESCRIPTION OF THE DRAWINGS

- [0015] The Figure is an illustration of a D logH characteristic curve.

DETAILED DESCRIPTION OF THE INVENTION

- 45 [0016] The invention has numerous advantages over prior practices in the art. The invention imaging elements provide the ability to have a single element that may be exposed with substantially invariant results over a wide range of exposure times. The photographic element of the invention when digitally exposed at exposure times of about 125 nanoseconds produces a clear, bright, and sharp image while minimizing fringing or other undesirable artifacts. The photographic element when digitally exposed maintains an acceptable maximum density in dark areas of the print, while also having the ability to print white whites in the white areas. The photographic element further has exceptional durability with great resistance to tearing and handling abuse which would deteriorate the image.
- 50 [0017] The optical performance of the photographic elements of the invention remains exceptional with optical exposure resulting in bright, sharp prints. It is a feature of this invention that prints made either optically or by digital exposure have substantially the same excellent characteristics. The color papers of the invention have excellent back-side characteristics with excellent writability, as well as the ability to be printed with multicolor indicia. The photographic element of the invention exhibits exceptional resistance to chemical degradation by environment gases such as oxides of nitrogen, commonly found in urban areas. The element of the invention also exhibits exceptional resistance to deg-
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radiation in image quality caused by exposure to sunlight or other sources of ultraviolet radiation. These and other advantages will be apparent from the detailed description below.

[0018] A full color photographic imaging element has at least one layer comprising a cyan dye forming coupler, one layer comprising a magenta dye forming coupler, and one layer comprising a yellow dye forming coupler and produces when developed an image in full color. Imaging layers are layers that contain sensitized silver halide and dye forming coupler.

[0019] In order to provide an imaging element that can be exposed in a negative working system and a direct writing sub microsecond digital system, a digitally capable emulsion set has been applied to a polyethylene coated cellulose paper base. It has been discovered quite surprisingly that the combination of dopants (i) and (ii) provides greater reduction in reciprocity law failure than can be achieved with either dopant alone. Further, unexpectedly, the combination of dopants (i) and (ii) achieve reductions in reciprocity law failure beyond the simple additive sum achieved when employing either dopant class by itself. It has not been reported or suggested prior to this invention that the combination of dopants (i) and (ii) provides greater reduction in reciprocity law failure, particularly for high intensity and short duration exposures. The combination of dopants (i) and (ii) further unexpectedly achieves high intensity reciprocity with iridium at relatively low levels, and both high and low intensity reciprocity improvements even while using conventional gelatino-peptizer (e.g., other than low methionine gelatino-peptizer).

[0020] The terms as used herein, "top", "upper", "emulsion side", "imaging side" and "face" mean the side or towards the side of an imaging member bearing the imaging layers or developed image. The terms "bottom", "lower side", and "back" mean the side or towards the side of the imaging member opposite from the side bearing the imaging layers or developed image. The term substrate as used herein refers to a support or base material that is the primary part of an imaging element such as paper, polyester, vinyl, synthetic paper, fabric, or other suitable material for the viewing of images. As used herein, the phrase "photographic element" is a material that utilizes photosensitive silver halide in the formation of images. The photographic elements are full color elements. Full color elements contain image dye-forming units sensitive to each of the three primary regions of the spectrum. Each unit can comprise a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer.

[0021] The photographic emulsions useful for this invention are generally prepared by precipitating silver halide crystals in a colloidal matrix by methods conventional in the art. The colloid is typically a hydrophilic film-forming agent such as gelatin, alginic acid, or derivatives thereof.

[0022] The crystals formed in the precipitation step are washed and then chemically and spectrally sensitized by adding spectral sensitizing dyes and chemical sensitizers, and by providing a heating step during which the emulsion temperature is raised, typically from 40°C to 70°C, and maintained for a period of time. The precipitation and spectral and chemical sensitization methods utilized in preparing the emulsions employed in the invention can be those methods known in the art.

[0023] The reflective support of the present invention preferably includes a resin layer with a stabilizing amount of hindered amine extruded on the top side of the imaging layer substrate. Hindered amine light stabilizers (HALS) originate from 2,2,6,6-tetramethylpiperidine. The hindered amine should be added to the polymer layer at about 0.01-5% by weight of said resin layer in order to provide resistance to polymer degradation upon exposure to UV light. The preferred amount is at about 0.05-3% by weight. This provides excellent polymer stability and resistance to cracking and yellowing while keeping the expense of the hindered amine to a minimum. Examples of suitable hindered amines with molecular weights of less than 2300 are Bis(2,2,6,6-tetramethyl-4-piperidiny)sebacate; Bis(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate; Bis(1,2,2,6,6-pentamethyl-4-piperidiny)2-n-butyl-(3,5-di-tert-butyl-hydroxybenzyl)malonate; 8-Acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro(4,5)decane-2,4-dione; Tetra(2,2,6,6-tetramethyl-4-piperidiny)1,2,3,4-butanetetracarboxylate; 1-(-2-[3,5-di-tert-butyl-4-hydroxyphenylpropionyloxy]ethyl)-4-(3,5-di-tert-butyl-4-hydroxyphenylpropionyloxy)-2,2,6,6-tetramethylpiperidine; 1,1'-(1,2-ethenediyl)bis(3,3,5,5-tetramethyl-2-piperazinone); The preferred hindered amine is 1,3,5-triazine-2,4,6-triamine,N,N"-[1,2-ethanediy]bis[[[4,6-bis(butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazine-2-yl)imino]-3,1 propanediyl]]-bis[N',N"-dibutyl-N',N"-bis(1,2,2,6,6-pentamethyl-4-piperidiny)] which will be referred to as Compound A. Compound A is preferred because when mixtures of polymers and Compound A are extruded onto imaging paper the polymer to paper adhesion is excellent and the long term stability of the imaging system against cracking and yellowing is improved.

[0024] Suitable polymers for the resin layer include polyethylene, polypropylene, polymethylpentene, polystyrene, polybutylene, and mixtures thereof. Polyolefin copolymers, including copolymers of polyethylene, propylene and ethylene such as hexene, butene, and octene are also useful. Polyethylene is most preferred, as it is low in cost and has desirable coating properties. As polyethylene, usable are high-density polyethylene, low-density polyethylene, linear low density polyethylene, and polyethylene blends. Other suitable polymers include polyesters produced from aromatic, aliphatic or cycloaliphatic dicarboxylic acids of 4-20 carbon atoms and aliphatic or alicyclic glycols having from 2-24 carbon atoms. Examples of suitable dicarboxylic acids include terephthalic, isophthalic, phthalic, naphthalene dicarboxylic

acid, succinic, glutaric, adipic, azelaic, sebacic, fumaric, maleic, itaconic, 1,4-cyclohexanedicarboxylic, sodiosulfisophthalic and mixtures thereof. Examples of suitable glycols include ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, 1,4-cyclohexanedimethanol, diethylene glycol, other polyethylene glycols and mixtures thereof. Other polymers are matrix polyesters having repeat units from terephthalic acid or naphthalene dicarboxylic acid and at least one glycol selected from ethylene glycol, 1,4-butanediol and 1,4-cyclohexanedimethanol such as poly(ethylene terephthalate), which may be modified by small amounts of other monomers. Other suitable polyesters include liquid crystal copolyesters formed by the inclusion of suitable amount of a co-acid component such as stilbene dicarboxylic acid. Examples of such liquid crystal copolyesters are those disclosed in U.S. Patent Nos. 4,420,607; 4,459,402; and 4,468,510. Useful polyamides include nylon 6, nylon 66, and mixtures thereof. Copolymers of polyamides are also suitable continuous phase polymers. An example of a useful polycarbonate is bisphenol-A polycarbonate. Cellulosic esters suitable for use as the continuous phase polymer of the composite sheets include cellulose nitrate, cellulose triacetate, cellulose diacetate, cellulose acetate propionate, cellulose acetate butyrate, and mixtures or copolymers thereof. Useful polyvinyl resins include polyvinyl chloride, poly(vinyl acetal), and mixtures thereof. Copolymers of vinyl resins can also be utilized.

[0025] Any suitable white pigment may be incorporated in the polyolefin layer, such as, for example, zinc oxide, zinc sulfide, zirconium dioxide, white lead, lead sulfate, lead chloride, lead aluminate, lead phthalate, antimony trioxide, white bismuth, tin oxide, white manganese, white tungsten, and combinations thereof. The preferred pigment is titanium dioxide because of its high refractive index, which gives excellent optical properties at a reasonable cost. The pigment is used in any form that is conveniently dispersed within the polyolefin. The preferred pigment is anatase titanium dioxide. The most preferred pigment is rutile titanium dioxide because it has the highest refractive index at the lowest cost. The average pigment diameter of the rutile TiO_2 is most preferably in the range of 0.1 to 0.26 μm . The pigments that are greater than 0.26 μm are too yellow for an imaging element application and the pigments that are less than 0.1 μm are not sufficiently opaque when dispersed in polymers. Preferably, the white pigment should be employed in the range of from about 10 to about 50 percent by weight, based on the total weight of the polyolefin coating. Below 10 percent TiO_2 , the imaging system will not be sufficiently opaque and will have inferior optical properties. Above 50 percent TiO_2 , the polymer blend is not manufacturable. The surface of the TiO_2 can be treated with an inorganic compounds such as aluminum hydroxide, alumina with a fluoride compound or fluoride ions, silica with a fluoride compound or fluoride ion, silicon hydroxide, silicon dioxide, boron oxide, boria-modified silica (as described in US Patent 4,781,761), phosphates, zinc oxide, ZrO_2 , etc. and with organic treatments such as polyhydric alcohol, polyhydric amine, metal soap, alkyl titanate, polysiloxanes, silanes, etc. The organic and inorganic TiO_2 treatments can be used alone or in any combination. The amount of the surface treating agents is preferably in the range of 0.2 to 2.0% for the inorganic treatment and 0.1 to 1% for the organic treatment, relative to the weight of the weight of the titanium dioxide. At these levels of treatment the TiO_2 disperses well in the polymer and does not interfere with the manufacture of the imaging support.

[0026] The polymer, hindered amine light stabilizer, and the TiO_2 are mixed with each other in the presence of a dispersing agent. Examples of dispersing agents are metal salts of higher fatty acids such as sodium palmitate, sodium stearate, calcium palmitate, sodium laurate, calcium stearate, aluminum stearate, magnesium stearate, zirconium octylate, zinc stearate, etc, higher fatty acids, higher fatty amide, and higher fatty acids. The preferred dispersing agent is sodium stearate and the most preferred dispersing agent is zinc stearate. Both of these dispersing agents give superior whiteness to the resin-coated layer.

[0027] For photographic use, a white base with a slight bluish tint is preferred. The layers of the waterproof resin coating preferably contain colorants such as a bluing agent and magenta or red pigment. Applicable bluing agents include commonly known ultramarine blue, cobalt blue, oxide cobalt phosphate, quinacridone pigments, and a mixture thereof. Applicable red or magenta colorants are quinacridones and ultramarines.

[0028] The resin may also include a fluorescing agent, which absorb energy in the UV region and emit light largely in the blue region. Any of the optical brighteners referred to in U.S. Patent 3,260,715 or a combination thereof would be beneficial.

[0029] The resin may also contain an antioxidant(s) such as hindered phenol primary antioxidants used alone or in combination with secondary antioxidants. Examples of hindered phenol primary antioxidants include pentaerythrityl tetraakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate] (such as Irganox 1010), octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (such as Irganox 1076 which will be referred to as compound B), benzenepropanoic acid 3,5-bis(1,1-dimethyl)-4-hydroxy-2-[3-(3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)-1-oxopropyl]hydrazide (such as Irganox MD1024), 2,2'-thiodiethylenebis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate] (such as Irganox 1035), 1,3,5-trimethyl-2,4,6-tri(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene (such as Irganox 1330), but are not limited to these examples. Secondary antioxidants include organic alkyl and aryl phosphites including examples such as triphenylphosphite (such as Irgastab TPP), tri(n-propylphenyl-phosphite) (such as Irgastab SN-55), 2,4-bis(1,1-dimethylphenyl) phosphite (such as Irgafos 168).

[0030] The hindered amine light stabilizer, TiO_2 , colorants, slip agents, optical brightener, and antioxidant are incorporated either together or separately with the polymer using a continuous or Banbury mixer. A concentrate of the addi-

tives in the form of a pellet is typically made. The concentration of the rutile pigment can be from 20% to 80% by weight of the masterbatch. The master batch is then adequately diluted for use with the resin.

[0031] The support to which the waterproof resin layer is laminated may be a polymeric, a synthetic paper, cloth, woven polymer fibers, or a cellulose fiber paper support, or laminates thereof. The base also may be a microvoided polyethylene terephthalate such as disclosed in U.S. Patent Nos. 4,912,333; 4,994,312; and 5,055,371. The preferred support is a photographic grade cellulose fiber paper.

[0032] To form the water-proof resin coating according to the present invention, the pellet containing the pigment and other additives is subjected to hot-melt coating onto a running support of paper or synthetic paper. If desired, the pellet is diluted with a polymer prior to hot melt coating. For a single layer coating the resin layer may be formed by lamination. The die is not limited to any specific type and may be any one of the common dies such as a T-slot or coat hanger die. An exit orifice temperature in heat melt extrusion of the water-proof resin ranges from 500-660°F. Further, before coating the support with resin, the support may be treated with an activating treatment such as corona discharge, flame, ozone, plasma, or glow discharge.

[0033] The thickness of the resin layer which is applied to a base paper of the reflective support used in the present invention at a side for imaging is preferably in the range of 5 to 100 μm , and most preferably in the range of 10 to 50 μm .

[0034] The thickness of the resin layer applied to a base paper on the side opposite the imaging element is preferably in a range from 5 to 100 μm and more preferably from 10 to 50 μm .

[0035] The surface of the waterproof resin coating at the imaging side may be a glossy, fine, silk, grain, or matte surface. On the surface of the water-proof coating on the backside which is not coated with an imaging element may also be glossy, fine, silk, or matte surface. The preferred water-proof surface for the backside away from the imaging element is matte.

[0036] This invention is directed to a silver halide photographic element capable of excellent performance when exposed by either an electronic printing method or a conventional optical printing method. An electronic printing method comprises subjecting a radiation sensitive silver halide emulsion layer of a recording element to actinic radiation of at least 10^{-4} ergs/cm² for up to 100 μ seconds duration in a pixel-by-pixel mode wherein the silver halide emulsion layer is comprised of silver halide grains as described above. A conventional optical printing method comprises subjecting a radiation sensitive silver halide emulsion layer of a recording element to actinic radiation of at least 10^{-4} ergs/cm² for 10^3 to 300 seconds in an imagewise mode wherein the silver halide emulsion layer is comprised of silver halide grains as described above.

[0037] This invention in a preferred embodiment utilizes a radiation-sensitive emulsion comprised of silver halide grains (a) containing greater than 50 mole percent chloride, based on silver, (b) having greater than 50 percent of their surface area provided by {100} crystal faces, and (c) having a central portion accounting for from 95 to 99 percent of total silver and containing two dopants selected to satisfy each of the following class requirements: (i) a hexacoordination metal complex which satisfies the formula



wherein n is zero, -1, -2, -3 or -4; M is a filled frontier orbital polyvalent metal ion, other than iridium; and L_6 represents bridging ligands which can be independently selected, provided that least four of the ligands are anionic ligands, and at least one of the ligands is a cyano ligand or a ligand more electronegative than a cyano ligand; and (ii) an iridium coordination complex containing a thiazole or substituted thiazole ligand.

[0038] This invention is directed towards a photographic recording element comprising a support and at least one light sensitive silver halide emulsion layer comprising silver halide grains as described above.

[0039] It has been discovered quite surprisingly that the combination of dopants (i) and (ii) provides greater reduction in reciprocity law failure than can be achieved with either dopant alone. Further, unexpectedly, the combination of dopants (i) and (ii) achieve reductions in reciprocity law failure beyond the simple additive sum achieved when employing either dopant class by itself. It has not been reported or suggested prior to this invention that the combination of dopants (i) and (ii) provides greater reduction in reciprocity law failure, particularly for high intensity and short duration exposures. The combination of dopants (i) and (ii) further unexpectedly achieves high intensity reciprocity with iridium at relatively low levels, and both high and low intensity reciprocity improvements even while using conventional gelatino-peptizer (e.g., other than low methionine gelatino-peptizer).

[0040] In a preferred practical application, the advantages of the invention can be transformed into increased throughput of digital substantially artifact-free color print images while exposing each pixel sequentially in synchronism with the digital data from an image processor.

[0041] In one embodiment, the present invention represents an improvement on the electronic printing method. Specifically, this invention in one embodiment is directed to an electronic printing method which comprises subjecting a radiation sensitive silver halide emulsion layer of a recording element to actinic radiation of at least 10^{-4} ergs/cm² for up to 100 μ seconds duration in a pixel-by-pixel mode. The present invention realizes an improvement in reciprocity fail-

ure by selection of the radiation sensitive silver halide emulsion layer. While certain embodiments of the invention are specifically directed towards electronic printing, use of the emulsions and elements of the invention is not limited to such specific embodiment, and it is specifically contemplated that the emulsions and elements of the invention are also well suited for conventional optical printing.

[0042] It has been unexpectedly discovered that significantly improved reciprocity performance can be obtained for silver halide grains (a) containing greater than 50 mole percent chloride, based on silver, and (b) having greater than 50 percent of their surface area provided by {100} crystal faces by employing a hexacoordination complex dopant of class (i) in combination with an iridium complex dopant comprising a thiazole or substituted thiazole ligand. The reciprocity improvement is obtained for silver halide grains employing conventional gelatino-peptizer, unlike the contrast improvement described for the combination of dopants set forth in U.S. Patents 5,783,373 and 5,783,378, which requires the use of low methionine gelatino-peptizers as discussed therein, and which states it is preferable to limit the concentration of any gelatino-peptizer with a methionine level of greater than 30 micromoles per gram to a concentration of less than 1 percent of the total peptizer employed. Accordingly, in specific embodiments of the invention, it is specifically contemplated to use significant levels (i.e., greater than 1 weight percent of total peptizer) of conventional gelatin (e.g., gelatin having at least 30 micromoles of methionine per gram) as a gelatino-peptizer for the silver halide grains of the emulsions of the invention. In preferred embodiments of the invention, gelatino-peptizer is employed which comprises at least 50 weight percent of gelatin containing at least 30 micromoles of methionine per gram, as it is frequently desirable to limit the level of oxidized low methionine gelatin which may be used for cost and certain performance reasons.

[0043] In a specific, preferred form of the invention it is contemplated to employ a class (i) hexacoordination complex dopant satisfying the formula:



where

n is zero, -1, -2, -3 or -4;

M is a filled frontier orbital polyvalent metal ion, other than iridium, preferably Fe^{+2} , Ru^{+2} , Os^{+2} , Co^{+3} , Rh^{+3} , Pd^{+4} or Pt^{+4} , more preferably an iron, ruthenium or osmium ion, and most preferably a ruthenium ion;

L_6 represents six bridging ligands which can be independently selected, provided that least four of the ligands are anionic ligands and at least one (preferably at least 3 and optimally at least 4) of the ligands is a cyano ligand or a ligand more electronegative than a cyano ligand. Any remaining ligands can be selected from among various other bridging ligands, including aquo ligands, halide ligands (specifically, fluoride, chloride, bromide and iodide), cyanate ligands, thiocyanate ligands, selenocyanate ligands, tellurocyanate ligands, and azide ligands. Hexacoordinated transition metal complexes of class (i) which include six cyano ligands are specifically preferred.

[0044] Illustrations of specifically contemplated class (i) hexacoordination complexes for inclusion in the high chloride grains are provided by Olm et al U.S. Patent 5,503,970 and Daubendiek et al U.S. Patents 5,494,789 and 5,503,971, and Keever et al U.S. Patent 4,945,035, as well as Murakami et al Japanese Patent Application Hei-2[1990]-249588, and *Research Disclosure* Item 36736. Useful neutral and anionic organic ligands for class (ii) dopant hexacoordination complexes are disclosed by Olm et al U.S. Patent 5,360,712 and Kuromoto et al U.S. Patent 5,462,849.

[0045] Class (i) dopant is preferably introduced into the high chloride grains after at least 50 (most preferably 75 and optimally 80) percent of the silver has been precipitated, but before precipitation of the central portion of the grains has been completed. Preferably class (i) dopant is introduced before 98 (most preferably 95 and optimally 90) percent of the silver has been precipitated. Stated in terms of the fully precipitated grain structure, class (i) dopant is preferably present in an interior shell region that surrounds at least 50 (most preferably 75 and optimally 80) percent of the silver and, with the more centrally located silver, accounts the entire central portion (99 percent of the silver), most preferably accounts for 95 percent, and optimally accounts for 90 percent of the silver halide forming the high chloride grains. The class (i) dopant can be distributed throughout the interior shell region delimited above or can be added as one or more bands within the interior shell region.

[0046] Class (i) dopant can be employed in any conventional useful concentration. A preferred concentration range is from 10^{-8} to 10^{-3} mole per silver mole, most preferably from 10^{-6} to 5×10^{-4} mole per silver mole.

[0047] The following are specific illustrations of class (i) dopants:

- (i-1) $[Fe(CN)_6]^{-4}$
- (i-2) $[Ru(CN)_6]^{-4}$
- (i-3) $[Os(CN)_6]^{-4}$
- (i-4) $[Rh(CN)_6]^{-3}$

- (i-5) $[\text{Co}(\text{CN})_6]^{-3}$
- (i-6) $[\text{Fe}(\text{pyrazine})(\text{CN})_5]^{-4}$
- (i-7) $[\text{RuCl}(\text{CN})_5]^{-4}$
- (i-8) $[\text{OsBr}(\text{CN})_5]^{-4}$
- 5 (i-9) $[\text{RhF}(\text{CN})_5]^{-3}$
- (i-10) $[\text{In}(\text{NCS})_6]^{-3}$
- (i-11) $[\text{FeCO}(\text{CN})_5]^{-3}$
- (i-12) $[\text{RuF}_2(\text{CN})_4]^{-4}$
- (i-13) $[\text{OsCl}_2(\text{CN})_4]^{-4}$
- 10 (i-14) $[\text{RhI}_2(\text{CN})_4]^{-3}$
- (i-15) $[\text{Ga}(\text{NCS})_6]^{-3}$
- (i-16) $[\text{Ru}(\text{CN})_5(\text{OCN})]^{-4}$
- (i-17) $[\text{Ru}(\text{CN})_5(\text{N}_3)]^{-4}$
- (i-18) $[\text{Os}(\text{CN})_5(\text{SCN})]^{-4}$
- 15 (i-19) $[\text{Rh}(\text{CN})_5(\text{SeCN})]^{-3}$
- (i-20) $[\text{Os}(\text{CN})\text{Cl}_5]^{-4}$
- (i-21) $[\text{Fe}(\text{CN})_3\text{Cl}_3]^{-3}$
- (i-22) $[\text{Ru}(\text{CO})_2(\text{CN})_4]^{-1}$

20 **[0048]** When the class (i) dopants have a net negative charge, it is appreciated that they are associated with a counter ion when added to the reaction vessel during precipitation. The counter ion is of little importance, since it is ionically dissociated from the dopant in solution and is not incorporated within the grain. Common counter ions known to be fully compatible with silver chloride precipitation, such as ammonium and alkali metal ions, are contemplated. It is noted that the same comments apply to class (ii) dopants, otherwise described below.

25 **[0049]** The class (ii) dopant is an iridium coordination complex containing at least one thiazole or substituted thiazole ligand. Careful scientific investigations have revealed Group VIII hexahalo coordination complexes to create deep electron traps, as illustrated R. S. Eachus, R. E. Graves and M. T. Olm *J. Chem. Phys.*, Vol. 69, pp. 4580-7 (1978) and *Physica Status Solidi A*, Vol. 57, 429-37 (1980) and R. S. Eachus and M. T. Olm *Annu. Rep. Prog. Chem. Sect. C. Phys. Chem.*, Vol. 83, 3, pp. 3-48 (1986). The class (ii) dopants employed in the practice of this invention are believed to create such deep electron traps. The thiazole ligands may be substituted with any photographically acceptable substituent which does not prevent incorporation of the dopant into the silver halide grain. Exemplary substituents include lower alkyl (e.g., alkyl groups containing 1-4 carbon atoms), and specifically methyl. A specific example of a substituted thiazole ligand which may be used in accordance with the invention is 5-methylthiazole. The class (ii) dopant preferably is an iridium coordination complex having ligands each of which are more electropositive than a cyano ligand. In a specifically preferred form the remaining non-thiazole or non-substituted-thiazole ligands of the coordination complexes forming class (ii) dopants are halide ligands.

[0050] It is specifically contemplated to select class (ii) dopants from among the coordination complexes containing organic ligands disclosed by Olm et al U.S. Patent 5,360,712, Olm et al U.S. Patent 5,457,021 and Kuromoto et al U.S. Patent 5,462,849.

40 **[0051]** In a preferred form it is contemplated to employ as a class (ii) dopant a hexacoordination complex satisfying the formula:

(II)



wherein

50 n' is zero, -1, -2, -3 or -4; and

L'_6 represents six bridging ligands which can be independently selected, provided that at least four of the ligands are anionic ligands, each of the the ligands is more electropositive than a cyano ligand, kind at least one of the ligands comprises a thiazole or substituted thiazole ligand. In a specifically preferred form at least four of the ligands are halide ligands, such as chloride or bromide ligands.

55 **[0052]** Class (ii) dopant is preferably introduced into the high chloride grains after at least 50 (most preferably 85 and optimally 90) percent of the silver has been precipitated, but before precipitation of the central portion of the grains has been completed. Preferably class (ii) dopant is introduced before 99 (most preferably 97 and optimally 95) percent

of the silver has been precipitated. Stated in terms of the fully precipitated grain structure, class (ii) dopant is preferably present in an interior shell region that surrounds at least 50 (most preferably 85 and optimally 90) percent of the silver and, with the more centrally located silver, accounts the entire central portion (99 percent of the silver), most preferably accounts for 97 percent, and optimally accounts for 95 percent of the silver halide forming the high chloride grains. The class (ii) dopant can be distributed throughout the interior shell region delimited above or can be added as one or more bands within the interior shell region.

[0053] Class (ii) dopant can be employed in any conventional useful concentration. A preferred concentration range is from 10^{-9} to 10^{-4} mole per silver mole. Iridium is most preferably employed in a concentration range of from 10^{-8} to 10^{-5} mole per silver mole.

[0054] Specific illustrations of class (ii) dopants are the following:

- (ii-1) $[\text{IrCl}_5(\text{thiazole})]^{-2}$
- (ii-2) $[\text{IrCl}_4(\text{thiazole})_2]^{-1}$
- (ii-3) $[\text{IrBr}_5(\text{thiazole})]^{-2}$
- (ii-4) $[\text{IrBr}_4(\text{thiazole})_2]^{-1}$
- (ii-5) $[\text{IrCl}_5(5\text{-methylthiazole})]^{-2}$
- (ii-6) $[\text{IrCl}_4(5\text{-methylthiazole})_2]^{-1}$
- (ii-7) $[\text{IrBr}_5(5\text{-methylthiazole})]^{-2}$
- (ii-8) $[\text{IrBr}_4(5\text{-methylthiazole})_2]^{-1}$

[0055] In one preferred aspect of the invention in a layer using a magenta dye forming coupler, a class (ii) dopant in combination with an $\text{OsCl}_5(\text{NO})$ dopant has been found to produce a preferred result.

[0056] Emulsions demonstrating the advantages of the invention can be realized by modifying the precipitation of conventional high chloride silver halide grains having predominantly (>50%) {100} crystal faces by employing a combination of class (i) and (ii) dopants as described above.

[0057] The silver halide grains precipitated contain greater than 50 mole percent chloride, based on silver. Preferably the grains contain at least 70 mole percent chloride and, optimally at least 90 mole percent chloride, based on silver. Iodide can be present in the grains up to its solubility limit, which is in silver iodochloride grains, under typical conditions of precipitation, about 11 mole percent, based on silver. It is preferred for most photographic applications to limit iodide to less than 5 mole percent iodide, most preferably less than 2 mole percent iodide, based on silver.

[0058] Silver bromide and silver chloride are miscible in all proportions. Hence, any portion, up to 50 mole percent, of the total halide not accounted for chloride and iodide, can be bromide. For color reflection print (i.e., color paper) uses bromide is typically limited to less than 10 mole percent based on silver and iodide is limited to less than 1 mole percent based on silver.

[0059] In a widely used form high chloride grains are precipitated to form cubic grains--that is, grains having {100} major faces and edges of equal length. In practice ripening effects usually round the edges and corners of the grains to some extent. However, except under extreme ripening conditions substantially more than 50 percent of total grain surface area is accounted for by {100} crystal faces.

[0060] High chloride tetradecahedral grains are a common variant of cubic grains. These grains contain 6 {100} crystal faces and 8 {111} crystal faces. Tetradecahedral grains are within the contemplation of this invention to the extent that greater than 50 percent of total surface area is accounted for by {100} crystal faces.

[0061] Although it is common practice to avoid or minimize the incorporation of iodide into high chloride grains employed in color paper, it has been recently observed that silver iodochloride grains with {100} crystal faces and, in some instances, one or more {111} faces offer exceptional levels of photographic speed. In these emulsions iodide is incorporated in overall concentrations of from 0.05 to 3.0 mole percent, based on silver, with the grains having a surface shell of greater than 50 Å that is substantially free of iodide and a interior shell having a maximum iodide concentration that surrounds a core accounting for at least 50 percent of total silver. Such grain structures are illustrated by Chen et al EPO 0 718 679.

[0062] In another improved form the high chloride grains can take the form of tabular grains having {100} major faces. Preferred high chloride {100} tabular grain emulsions are those in which the tabular grains account for at least 70 (most preferably at least 90) percent of total grain projected area. Preferred high chloride {100} tabular grain emulsions have average aspect ratios of at least 5 (most preferably at least >8). Tabular grains typically have thicknesses of less than 0.3 µm, preferably less than 0.2 µm, and optimally less than 0.07 µm. High chloride {100} tabular grain emulsions and their preparation are disclosed by Maskasky U.S. Patents 5,264,337 and 5,292,632, House et al U.S. Patent 5,320,938, Brust et al U.S. Patent 5,314,798 and Chang et al U.S. Patent 5,413,904.

[0063] Once high chloride grains having predominantly {100} crystal faces have been precipitated with a combination of class (i) and class (ii) dopants described above, chemical and spectral sensitization, followed by the addition of conventional addenda to adapt the emulsion for the imaging application of choice can take any convenient conventional

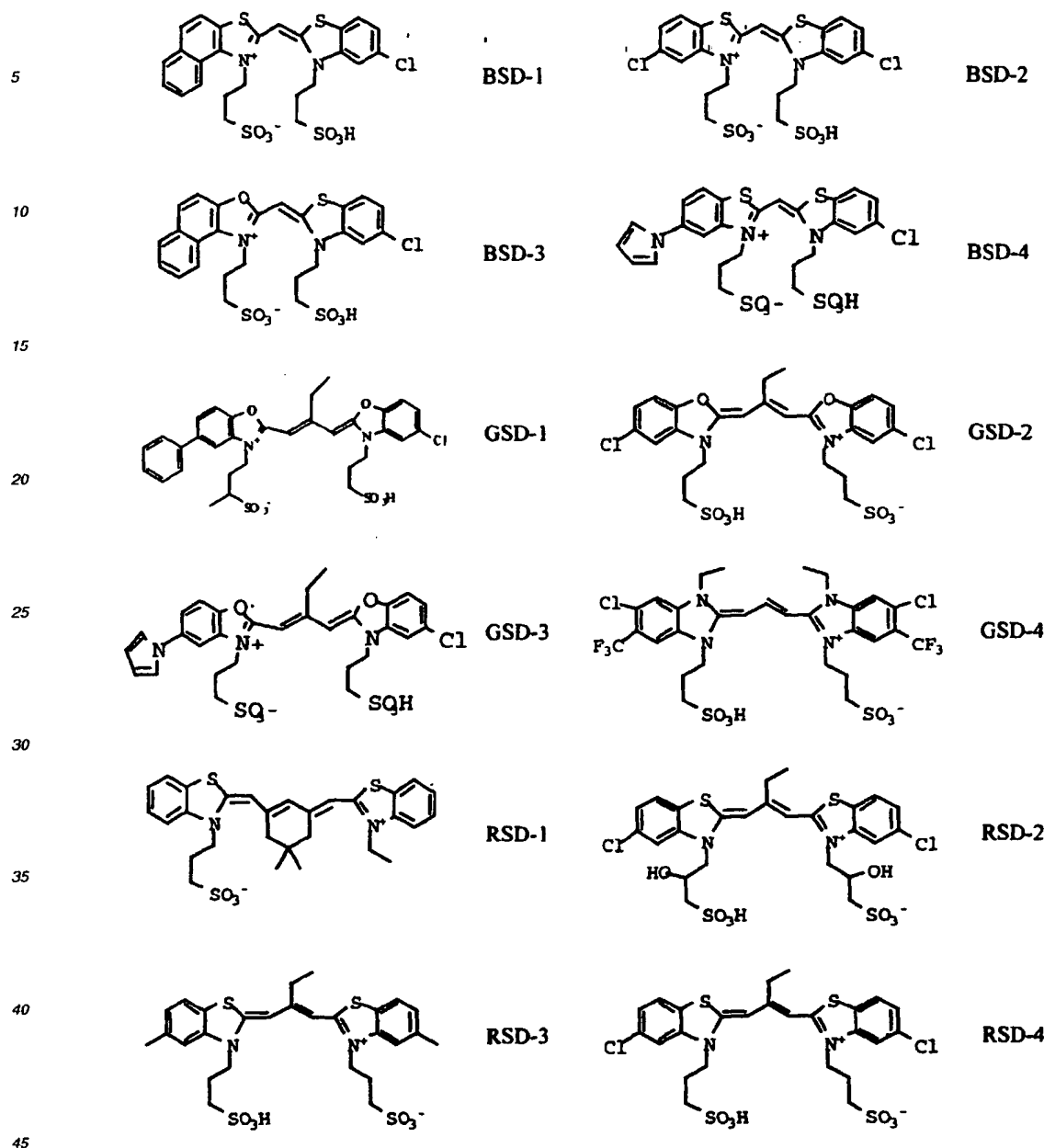
form. These conventional features are illustrated by *Research Disclosure*, Item 38957, cited above, particularly:

- III. Emulsion washing;
- IV. Chemical sensitization;
- 5 V. Spectral sensitization and desensitization;
- VII. Antifoggants and stabilizers;
- VIII. Absorbing and scattering materials;
- IX. Coating and physical property modifying addenda; and
- 10 X. Dye image formers and modifiers.

[0064] Some additional silver halide, typically less than 1 percent, based on total silver, can be introduced to facilitate chemical sensitization. It is also recognized that silver halide can be epitaxially deposited at selected sites on a host grain to increase its sensitivity. For example, high chloride {100} tabular grains with corner epitaxy are illustrated by Maskasky U.S. Patent 5,275,930. For the purpose of providing a clear demarcation, the term "silver halide grain" is
 15 herein employed to include the silver necessary to form the grain up to the point that the final {100} crystal faces of the grain are formed. Silver halide later deposited that does not overlie the {100} crystal faces previously formed accounting for at least 50 percent of the grain surface area is excluded in determining total silver forming the silver halide grains. Thus, the silver forming selected site epitaxy is not part of the silver halide grains while silver halide that deposits and provides the final {100} crystal faces of the grains is included in the total silver forming the grains, even when it differs
 20 significantly in composition from the previously precipitated silver halide.

[0065] The emulsions can be spectrally sensitized with any of the dyes known to the photographic art, such as the polymethine dye class, which includes the cyanines, merocyanines, complex cyanines and merocyanines, oxonols, hemioxonols, styryls, merostyryls and streptocyanines. In particular, it would be advantageous to select from among the
 25 low staining sensitizing dyes disclosed in U.S. Patents 5,292,634; 5,316,904; 5,418,126 and 5,492,802. Use of low staining sensitizing dyes in a photographic element processed in a developer solution with little or no optical brightening agent (for instance, stilbene compounds such as Blankophor REU™) is specifically contemplated. Further, these low staining dyes can be used in combination with other dyes known to the art (*Research Disclosure*, September 1996, Item 38957, Section V).

[0066] Useful sensitizing dyes include, but are not limited to, the following.



[0067] Emulsions can be spectrally sensitized with mixtures of two or more sensitizing dyes which form mixed dye aggregates on the surface of the emulsion grain. The use of mixed dye aggregates enables adjustment of the spectral sensitivity of the emulsion to any wavelength between the extremes of the wavelengths of peak sensitivities (λ -max) of the two or more dyes. This practice is especially valuable if the two or more sensitizing dyes absorb in similar portions of the spectrum (i.e., blue, or green or red and not green plus red or blue plus red or green plus blue). Since the function of the spectral sensitizing dye is to modulate the information recorded in the negative which is recorded as an image dye, positioning the peak spectral sensitivity at or near the λ -max of the image dye in the color negative produces the optimum preferred response. In addition, the combination of similarly spectrally sensitized emulsions can be in one or more layers.

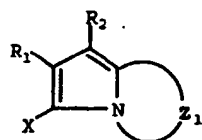
[0068] An important quality characteristic of a reproductive film system is color reproduction, which represents how accurately the hues of the original scene are reproduced. Many current color papers use a blue sensitizing dye that

gives a maximum sensitivity at about 480 nm. Use of a sensitizing dye that affords a sensitivity maximum that is closer to that of the yellow image dye in film, for instance with a sensitivity maximum of around 450-470 nm, can result in a color paper with improved color reproduction.

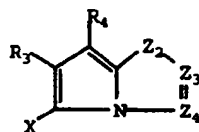
[0069] In the simplest contemplated form a recording element contemplated for use in the electronic printing method of one embodiment of the invention can consist of a single emulsion layer satisfying the emulsion description provided above coated on a conventional photographic support, such as those described in *Research Disclosure*, Item 38957, cited above, XVI. Supports. In one preferred form the support is a white reflective support, such as photographic paper support or a film support that contains or bears a coating of a reflective pigment. To permit a print image to be viewed using an illuminant placed behind the support, it is preferred to employ a white translucent support, such as a Duratrans™ or Duraclear™ support.

[0070] Image dye-forming couplers may be included in the element such as couplers that form cyan dyes upon reaction with oxidized color developing agents which are described in such representative patents and publications as: U.S. Patent Nos. 2,367,531; 2,423,730; 2,474,293; 2,772,162; 2,895,826; 3,002,836; 3,034,892; 3,041,236; 4,883,746 and "Farbkuppler - Eine Literature Übersicht," published in *Agfa Mitteilungen*, Band III, pp. 156-175 (1961). Preferably such couplers are phenols and naphthols that form cyan dyes on reaction with oxidized color developing agent. Also preferable are the cyan couplers described in, for instance, European Patent Application Nos. 491,197; 544,322; 556,700; 556,777; 565,096; 570,006; and 574,948.

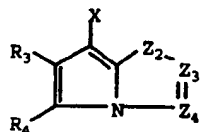
[0071] Typical cyan couplers are represented by the following formulas:



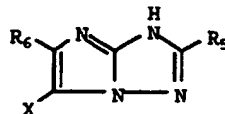
CYAN-1



CYAN-2



CYAN-3



CYAN-4

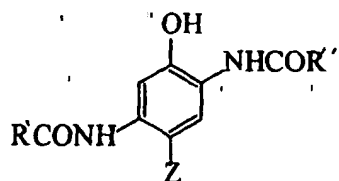
wherein R_1 , R_5 and R_8 each represents a hydrogen or a substituent; R_2 represents a substituent; R_3 , R_4 , and R_7 each represents an electron attractive group having a Hammett's substituent constant σ_{para} of 0.2 or more and the sum of the σ_{para} values of R_3 and R_4 is 0.65 or more; R_6 represents an electron attractive group having a Hammett's substituent constant σ_{para} of 0.35 or more; X represents a hydrogen or a coupling-off group; Z_1 represents nonmetallic atoms necessary for forming a nitrogen-containing, six-membered, heterocyclic ring which has at least one dissociative group; Z_2 represents $-C(R_7)=$ and $-N=$; and Z_3 and Z_4 each represent $-C(R_8)=$ and $-N=$.

[0072] For purposes of this invention, an "NB coupler" is a dye-forming coupler which is capable of coupling with the developer 4-amino-3-methyl-N-ethyl-N-(2-methanesulfonamidoethyl) aniline sesquisulfate hydrate to form a dye for which the left bandwidth (LBW) of its absorption spectra upon "spin coating" of a 3% w/v solution of the dye in di-n-butyl sebacate solvent is at least 5 nm. less than the LBW for a 3% w/v solution of the same dye in acetonitrile. The LBW of the spectral curve for a dye is the distance between the left side of the spectral curve and the wavelength of maximum absorption measured at a density of half the maximum.

[0073] The "spin coating" sample is prepared by first preparing a solution of the dye in di-n-butyl sebacate solvent (3% w/v). If the dye is insoluble, dissolution is achieved by the addition of some methylene chloride. The solution is filtered and 0.1-0.2ml is applied to a clear polyethylene terephthalate support (approximately 4cm x 4cm) and spun at 4,000RPM using the Spin Coating equipment, Model No. EC101, available from Headway Research Inc., Garland TX. The transmission spectra of the so prepared dye samples are then recorded.

[0074] Preferred "NB couplers" form a dye which, in n-butyl sebacate, has a LBW of the absorption spectra upon "spin coating" which is at least 15 nm, preferably at least 25 nm, less than that of the same dye in a 3% solution (w/v) in acetonitrile.

[0075] In a preferred embodiment the cyan dye-forming "NB coupler" useful in the invention has the formula (IA)



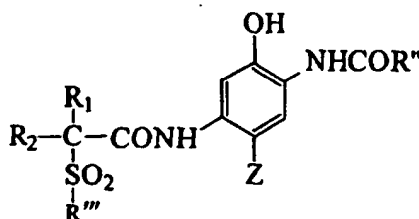
(IA)

wherein

R' and R'' are substituents selected such that the coupler is a "NB coupler", as herein defined; and Z is a hydrogen atom or a group which can be split off by the reaction of the coupler with an oxidized color developing agent.

[0076] The coupler of formula (IA) is a 2,5-diamido phenolic cyan coupler wherein the substituents R' and R'' are preferably independently selected from unsubstituted or substituted alkyl, aryl, amino, alkoxy and heterocyclyl groups.

[0077] In a further preferred embodiment, the "NB coupler" has the formula (I):



(I)

wherein

R'' and R''' are independently selected from unsubstituted or substituted alkyl, aryl, amino, alkoxy and heterocyclyl groups and Z is as hereinbefore defined;

R₁ and R₂ are independently hydrogen or an unsubstituted or substituted alkyl group; and

Typically, R'' is an alkyl, amino or aryl group, suitably a phenyl group. R''' is desirably an alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring group is unsubstituted or substituted.

[0078] In the preferred embodiment the coupler of formula (I) is a 2,5-diamido phenol in which the 5-amido moiety is an amide of a carboxylic acid which is substituted in the alpha position by a particular sulfone (-SO₂-) group, such as, for example, described in U.S. Patent No. 5,686,235. The sulfone moiety is an unsubstituted or substituted alkylsulfone or a heterocyclyl sulfone or it is an arylsulfone, which is preferably substituted, in particular in the meta and/or para position.

[0079] Couplers having these structures of formulae (I) or (IA) comprise cyan dye-forming "NB couplers" which form image dyes having very sharp-cutting dye hues on the short wavelength side of the absorption curves with absorption maxima (λ_{max}) which are shifted hypsochromically and are generally in the range of 620-645 nm, which is ideally suited for producing excellent color reproduction and high color saturation in color photographic papers.

[0080] Referring to formula (I), R₁ and R₂ are independently hydrogen or an unsubstituted or substituted alkyl group, preferably having from 1 to 24 carbon atoms and in particular 1 to 10 carbon atoms, suitably a methyl, ethyl, n-propyl, isopropyl, butyl or decyl group or an alkyl group substituted with one or more fluoro, chloro or bromo atoms, such as a trifluoromethyl group. Suitably, at least one of R₁ and R₂ is a hydrogen atom and if only one of R₁ and R₂ is a hydrogen atom then the other is preferably an alkyl group having 1 to 4 carbon atoms, more preferably one to three carbon atoms and desirably two carbon atoms.

[0081] As used herein and throughout the specification unless where specifically stated otherwise, the term "alkyl" refers to an unsaturated or saturated straight or branched chain alkyl group, including alkenyl, and includes aralkyl and cyclic alkyl groups, including cycloalkenyl, having 3-8 carbon atoms and the term 'aryl' includes specifically fused aryl.

[0082] In formula (I), R¹ is suitably an unsubstituted or substituted amino, alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted, but is more suitably an unsubstituted or substituted phenyl group.

[0083] Examples of suitable substituent groups for this aryl or heterocyclic ring include cyano, chloro, fluoro, bromo, iodo, alkyl- or aryl-carbonyl, alkyl- or aryl-oxycarbonyl, carbonamido, alkyl- or aryl-carbonamido, alkyl- or aryl-sulfonyl, alkyl- or aryl-sulfonyloxy, alkyl- or aryl-oxysulfonyl, alkyl- or aryl-sulfoxide, alkyl- or aryl-sulfamoyl, alkyl- or aryl-sulfonamido, aryl, alkyl, alkoxy, aryloxy, nitro, alkyl- or aryl-ureido and alkyl- or aryl-carbamoyl groups, any of which may be further substituted. Preferred groups are halogen, cyano, alkoxycarbonyl, alkylsulfamoyl, alkyl-sulfonamido, alkylsulfonyl, carbamoyl, alkylcarbamoyl or alkylcarbonamido. Suitably, R¹ is a 4-chlorophenyl, 3,4-di-chlorophenyl, 3,4-difluorophenyl, 4-cyanophenyl, 3-chloro-4-cyanophenyl, pentafluorophenyl, or a 3- or 4-sulfonamidophenyl group.

[0084] In formula (I), when R¹ is alkyl it may be unsubstituted or substituted with a substituent such as halogen or alkoxy. When R¹ is aryl or a heterocycle, it may be substituted. Desirably it is not substituted in the position alpha to the sulfonyl group.

[0085] In formula (I), when R¹ is a phenyl group, it may be substituted in the meta and/or para positions with one to three substituents independently selected from the group consisting of halogen, and unsubstituted or substituted alkyl, alkoxy, aryloxy, acyloxy, acylamino, alkyl- or aryl-sulfonyloxy, alkyl- or aryl-sulfamoyl, alkyl- or aryl-sulfamoylamino, alkyl- or aryl-sulfonamido, alkyl- or aryl-ureido, alkyl- or aryl-oxycarbonyl, alkyl- or aryl-oxy-carbonylamino and alkyl- or aryl-carbamoyl groups.

[0086] In particular each substituent may be an alkyl group such as methyl, t-butyl, heptyl, dodecyl, pentadecyl, octadecyl or 1,1,2,2-tetramethylpropyl; an alkoxy group such as methoxy, t-butoxy, octyloxy, dodecyloxy, tetradecyloxy, hexadecyloxy or octadecyloxy; an aryloxy group such as phenoxy, 4-t-butylphenoxy or 4-dodecyl-phenoxy; an alkyl- or aryl-acyloxy group such as acetoxyl or dodecanoyloxy; an alkyl- or aryl-acylamino group such as acetamido, hexadecanamido or benzamido; an alkyl- or aryl-sulfonyloxy group such as methyl-sulfonyloxy, dodecylsulfonyloxy or 4-methyl-phenyl-sulfonyloxy; an alkyl- or aryl-sulfamoyl-group such as N-butylsulfamoyl or N-4-t-butylphenylsulfamoyl; an alkyl- or aryl-sulfamoylamino group such as N-butyl-sulfamoylamino or N-4-t-butylphenylsulfamoyl-amino; an alkyl- or aryl-sulfonamido group such as methane-sulfonamido, hexadecanesulfonamido or 4-chlorophenyl-sulfonamido; an alkyl- or aryl-ureido group such as methylureido or phenylureido; an alkoxy- or aryloxy-carbonyl such as methoxycarbonyl or phenoxy-carbonyl; an alkoxy- or aryloxy-carbonylamino group such as methoxycarbonylamino or phenoxy-carbonylamino; an alkyl- or aryl-carbamoyl group such as N-butylcarbamoyl or N-methyl-N-dodecylcarbamoyl; or a perfluor-alkyl group such as trifluoromethyl or heptafluoropropyl.

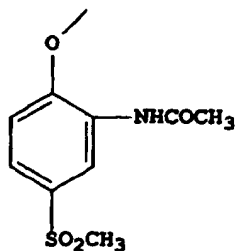
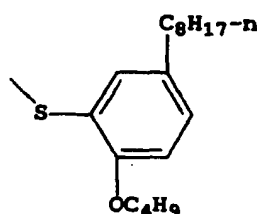
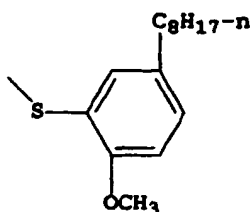
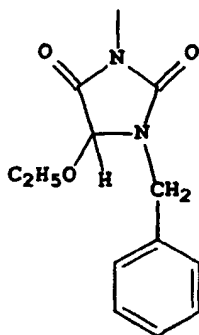
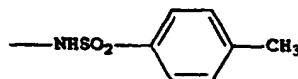
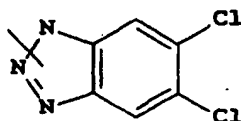
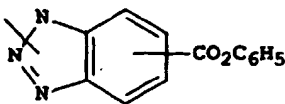
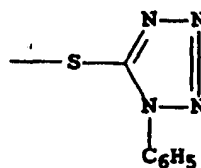
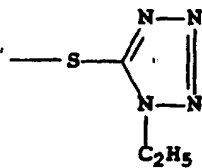
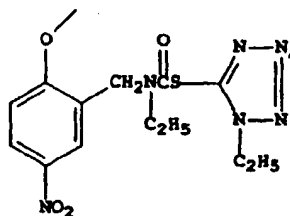
[0087] Suitably the above substituent groups have 1 to 30 carbon atoms, more preferably 8 to 20 aliphatic carbon atoms. A desirable substituent is an alkyl group of 12 to 18 aliphatic carbon atoms such as dodecyl, pentadecyl or octadecyl or an alkoxy group with 8 to 18 aliphatic carbon atoms such as dodecyloxy and hexadecyloxy or a halogen such as a meta or para chloro group, carboxy or sulfonamido. Any such groups may contain interrupting heteroatoms such as oxygen to form e.g. polyalkylene oxides.

[0088] In formula (I) or (IA) Z is a hydrogen atom or a group which can be split off by the reaction of the coupler with an oxidized color developing agent, known in the photographic art as a 'coupling-off group' and may preferably be hydrogen, chloro, fluoro, substituted aryloxy or mercaptotetrazole, more preferably hydrogen or chloro.

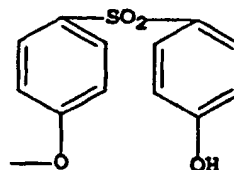
[0089] The presence or absence of such groups determines the chemical equivalency of the coupler, i.e., whether it is a 2-equivalent or 4-equivalent coupler, and its particular identity can modify the reactivity of the coupler. Such groups can advantageously affect the layer in which the coupler is coated, or other layers in the photographic recording material, by performing, after release from the coupler, functions such as dye formation, dye hue adjustment, development acceleration or inhibition, bleach acceleration or inhibition, electron transfer facilitation, color correction, and the like.

[0090] Representative classes of such coupling-off groups include, for example, halogen, alkoxy, aryloxy, heterocyclyloxy, sulfonyloxy, acyloxy, acyl, heterocyclylsulfonamido, heterocyclylthio, benzothiazolyl, phosphonyloxy, alkylthio, arylthio, and arylazo. These coupling-off groups are described in the art, for example, in U.S. Patent Nos. 2,455,169; 3,227,551; 3,432,521; 3,467,563; 3,617,291; 3,880,661; 4,052,212; and 4,134,766; and in U.K. Patent Nos. and published applications 1,466,728; 1,531,927; 1,533,039; 2,066,755A, and 2,017,704A. Halogen, alkoxy and aryloxy groups are most suitable.

[0091] Examples of specific coupling-off groups are -Cl, -F, -Br, -SCN, -OCH₃, -OC₆H₅, -OCH₂C(=O)NHCH₂CH₂OH, -OCH₂C(=O)NHCH₂CH₂OCH₃, -OCH₂C(=O)NHCH₂CH₂OC(=O)OCH₃, -P(=O)(OC₂H₅)₂, -SCH₂CH₂COOH,



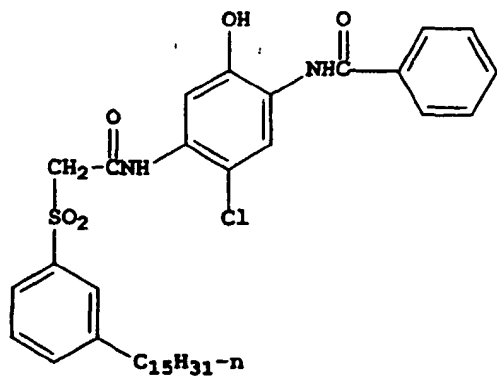
, and



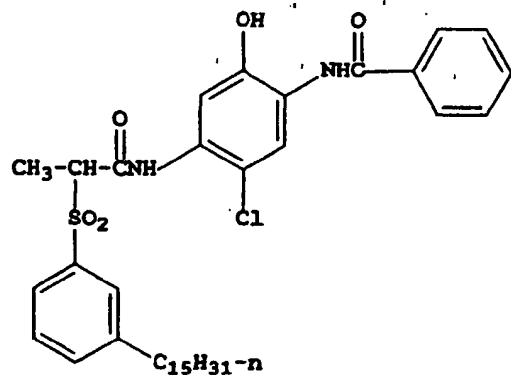
[0092] Typically, the coupling-off group is a chlorine atom, hydrogen atom or p-methoxyphenoxy group.

[0093] It is essential that the substituent groups be selected so as to adequately ballast the coupler and the resulting dye in the organic solvent in which the coupler is dispersed. The ballasting may be accomplished by providing hydrophobic substituent groups in one or more of the substituent groups. Generally a ballast group is an organic radical of such size and configuration as to confer on the coupler molecule sufficient bulk and aqueous insolubility as to render the coupler substantially nondiffusible from the layer in which it is coated in a photographic element. Thus, the combination of substituent are suitably chosen to meet these criteria. To be effective, the ballast will usually contain at least 8 carbon atoms and typically contains 10 to 30 carbon atoms. Suitable ballasting may also be accomplished by providing a plurality of groups which in combination meet these criteria. In the preferred embodiments of the invention R_1 in formula (I) is a small alkyl group or hydrogen. Therefore, in these embodiments the ballast would be primarily located as part of the other groups. Furthermore, even if the coupling-off group Z contains a ballast it is often necessary to ballast the other substituents as well, since Z is eliminated from the molecule upon coupling; thus, the ballast is most advantageously provided as part of groups other than Z.

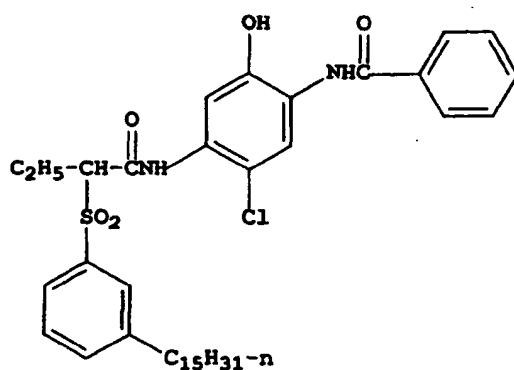
[0094] The following examples further illustrate preferred coupler of the invention. It is not to be construed that the present invention is limited to these examples.



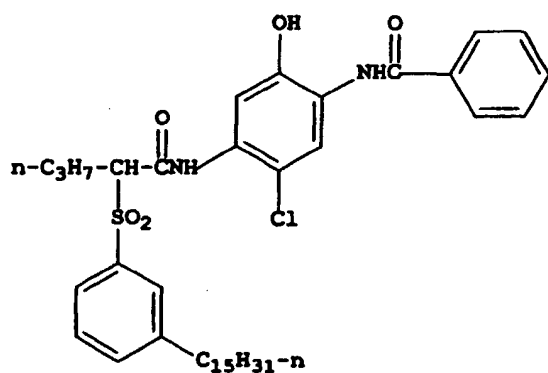
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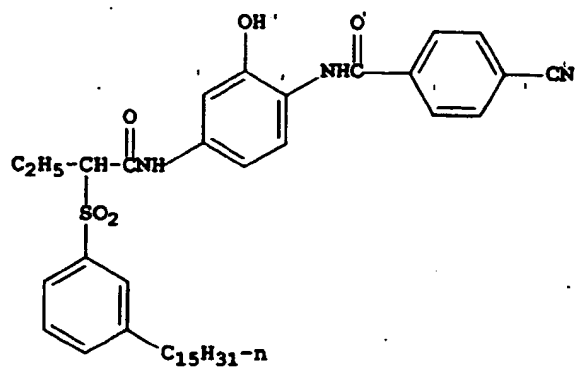
IC-2



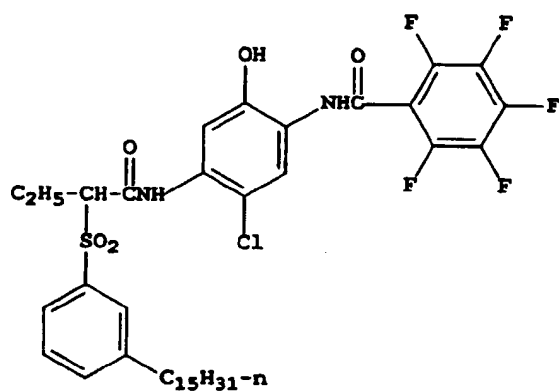
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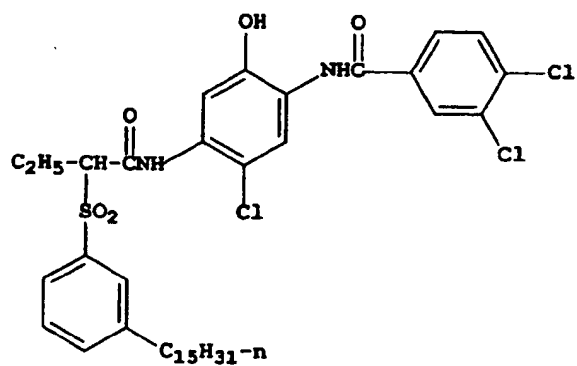
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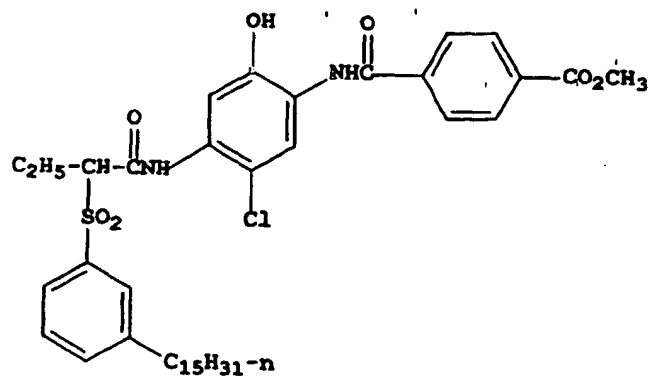
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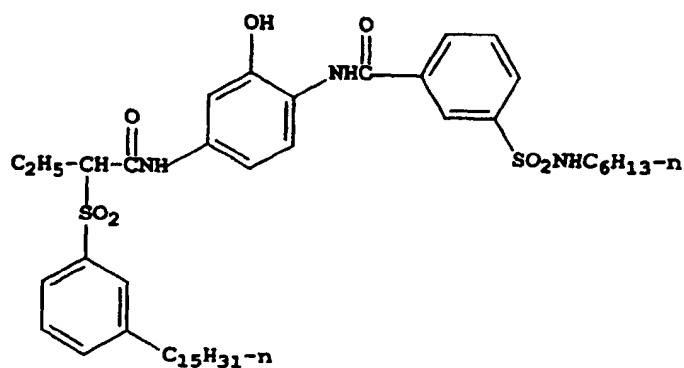
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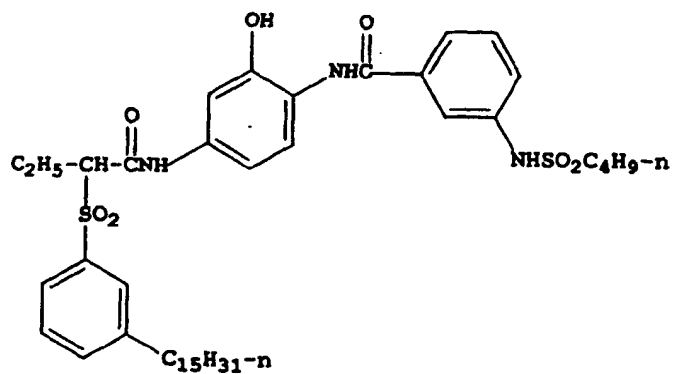
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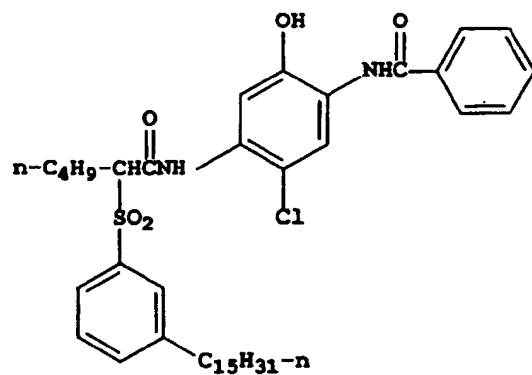
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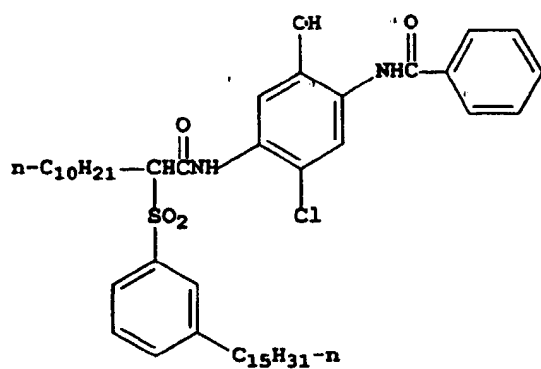


IC-9

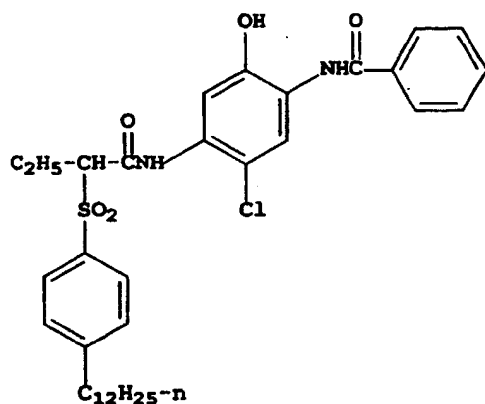


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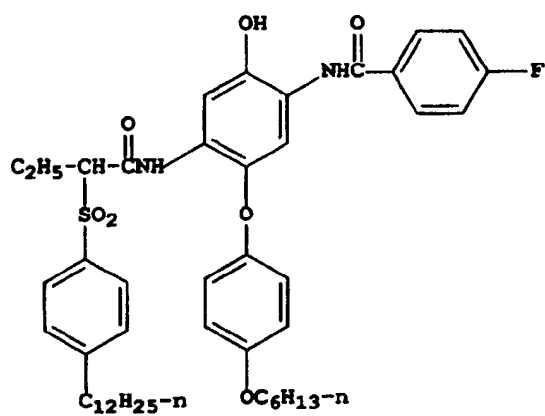




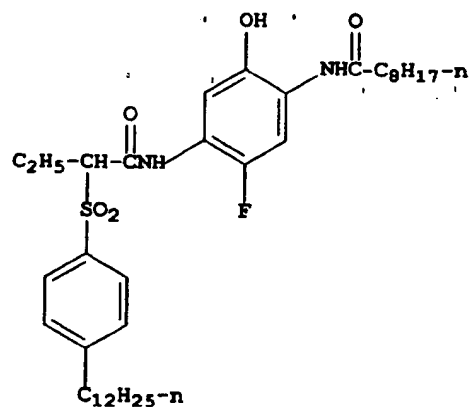
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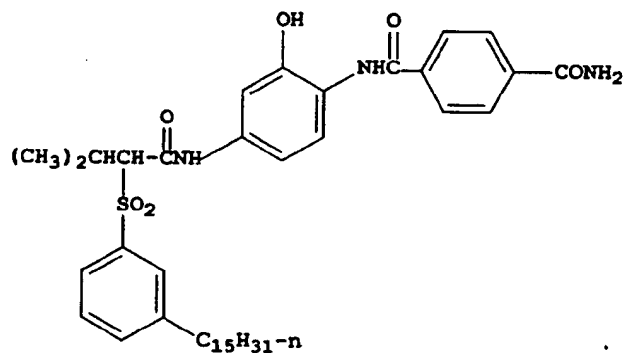
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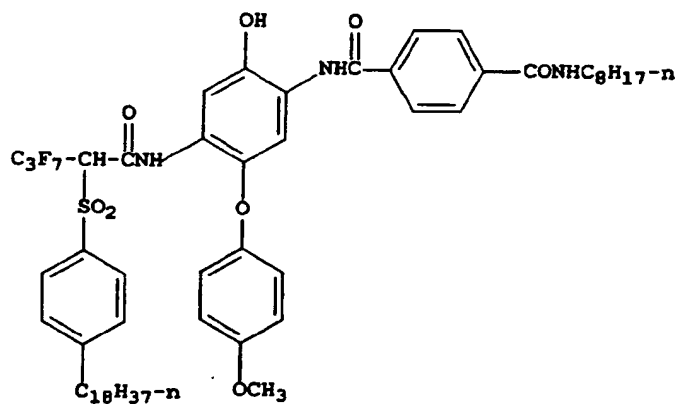
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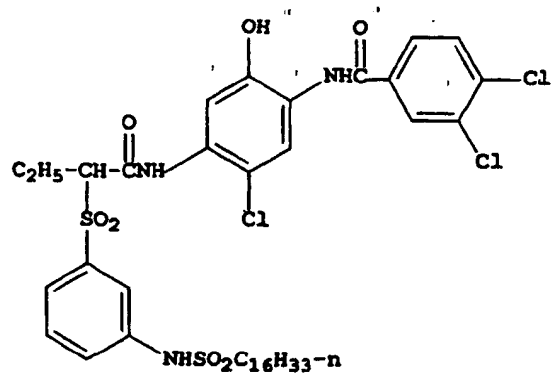
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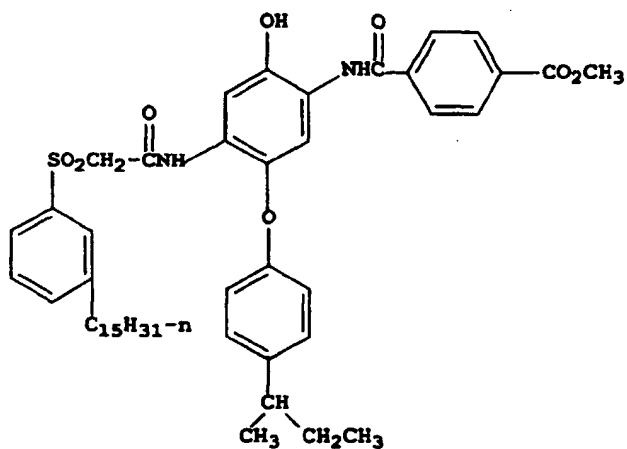
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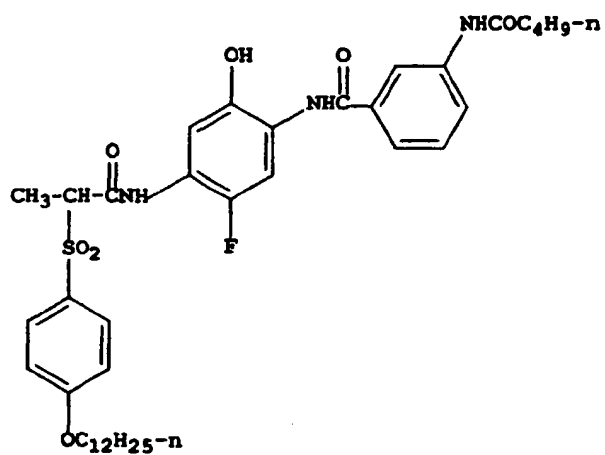
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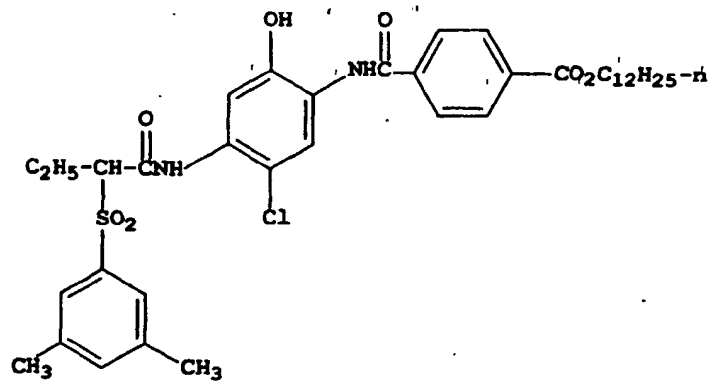
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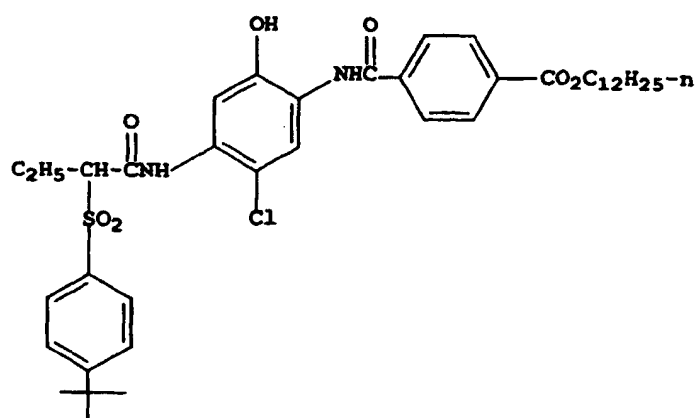
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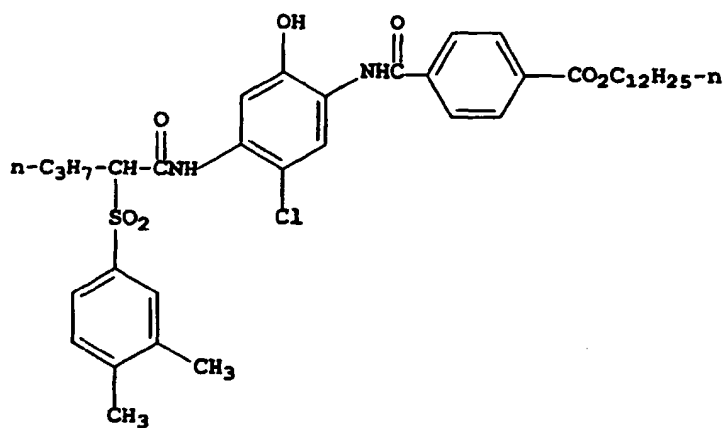
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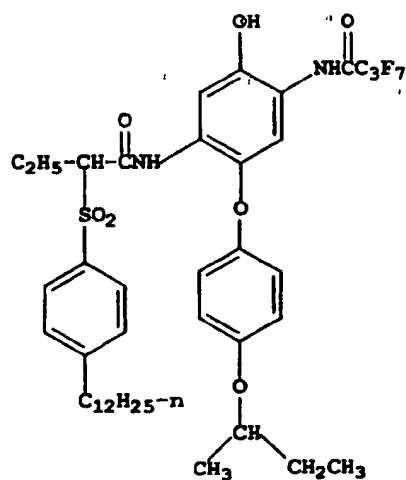
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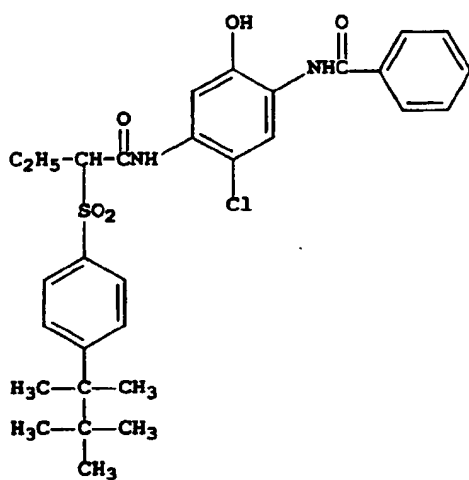
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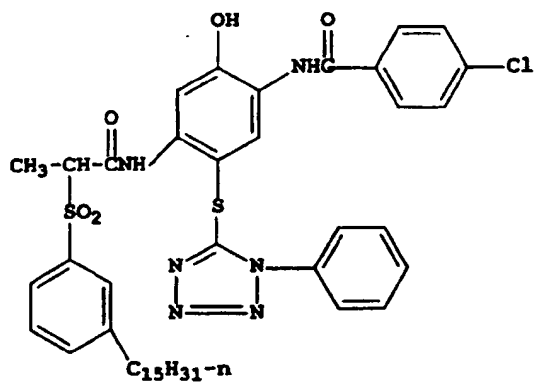
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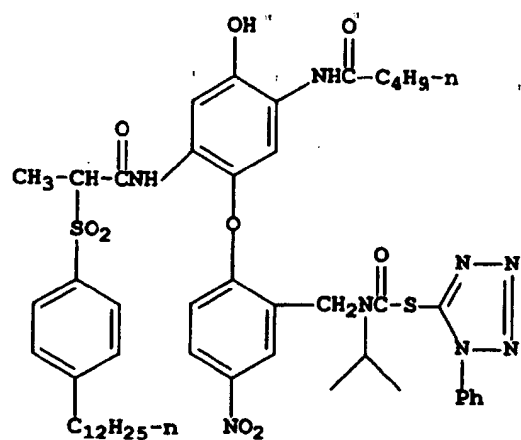
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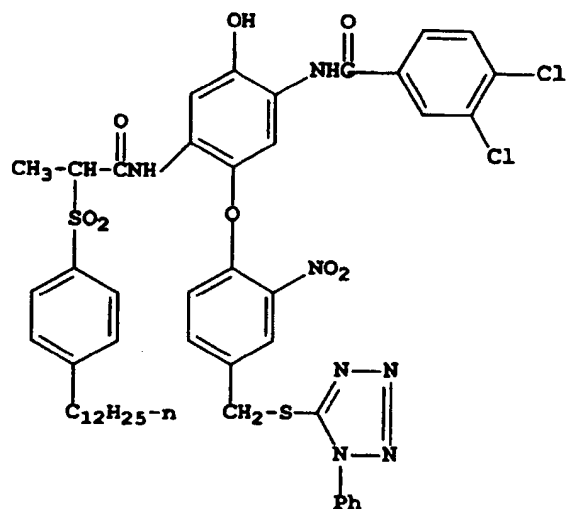
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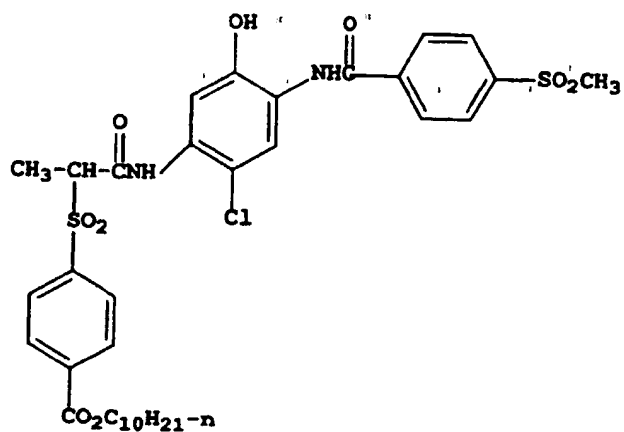
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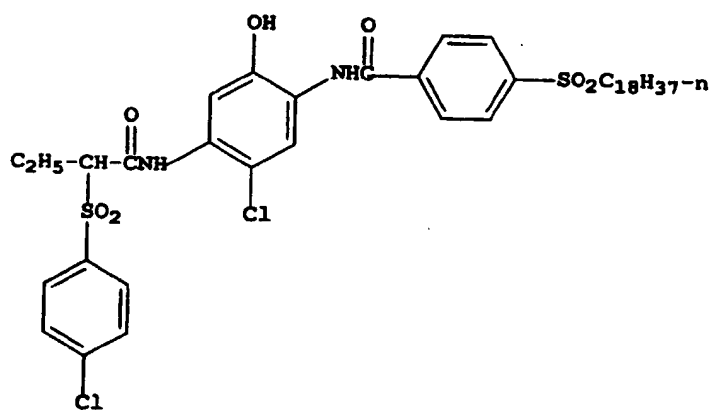
IC-29



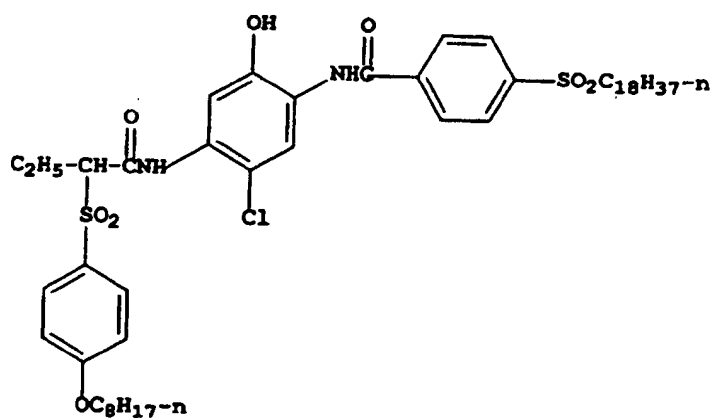
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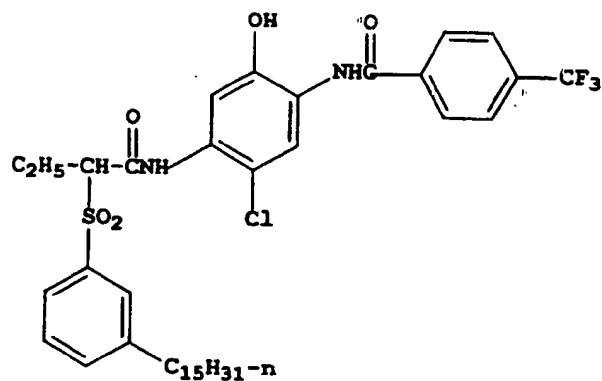
IC-31



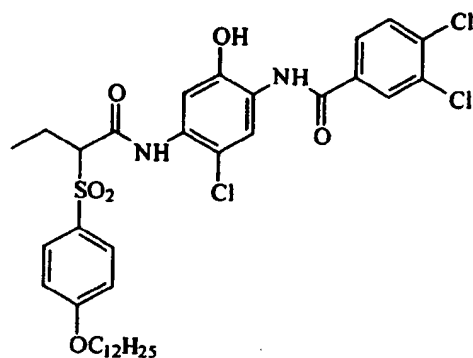
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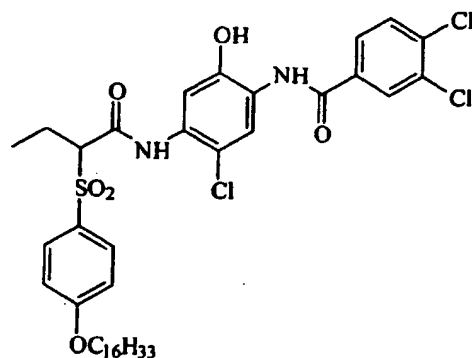
IC-33



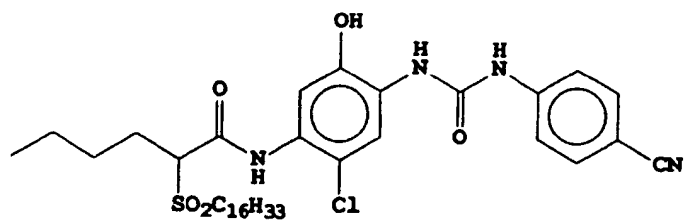
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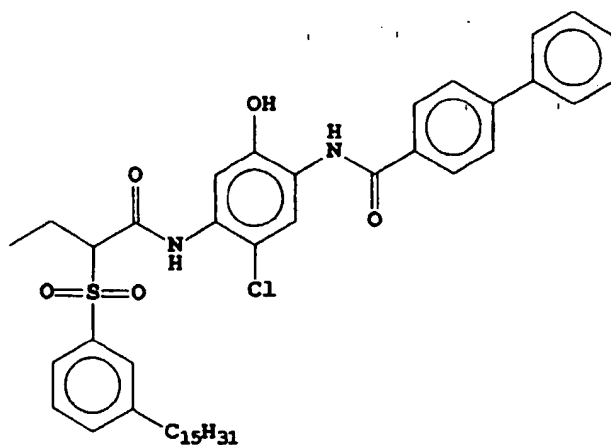
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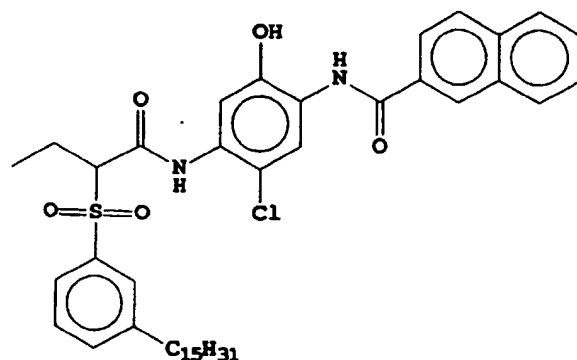
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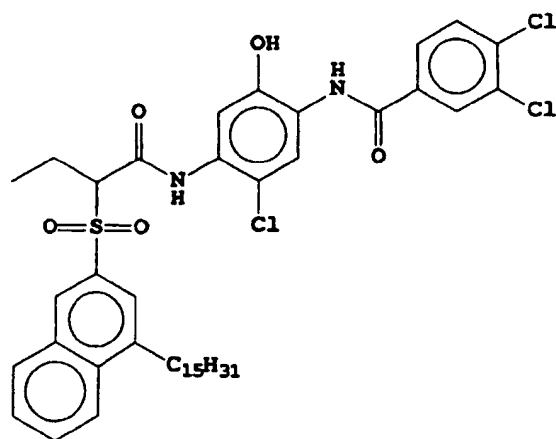
IC-37



IC-38



IC-39



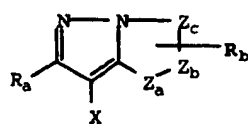
IC-40

[0095] Preferred couplers are IC-3, IC-7, IC-35, and IC-36 because of their suitably narrow left bandwidths.

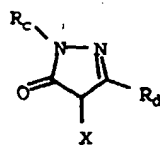
[0096] Couplers that form magenta dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Patent Nos. 2,311,082; 2,343,703; 2,369,489; 2,600,788; 2,908,573; 3,062,653; 3,152,896; 3,519,429; 3,758,309, and "Farbkuppler-eine Literature Übersicht," published in Agfa Mitteilungen, Band III, pp. 126-156 (1961). Preferably such couplers are pyrazolones, pyrazolotriazoles, or pyrazolobenzimidazoles that form magenta dyes upon reaction with oxidized color developing agents. Especially preferred couplers are 1H-pyrazolo [5,1-c]-1,2,4-triazole and 1H-pyrazolo [1,5-b]-1,2,4-triazole. Examples of 1H-pyrazolo [5,1-c]-1,2,4-triazole couplers are described in U.K. Patent Nos. 1,247,493; 1,252,418; 1,398,979; U.S. Patent Nos. 4,443,536; 4,514,490; 4,540,654; 4,590,153; 4,665,015; 4,822,730; 4,945,034; 5,017,465; and 5,023,170. Examples of 1H-pyrazolo [1,5-b]-1,2,4-triazoles can be found in European Patent applications 176,804; 177,765; U.S. Patent Nos. 4,659,652; 5,066,575;

and 5,250,400.

[0097] Typical pyrazoloazole and pyrazolone couplers are represented by the following formulas:



MAGENTA-1

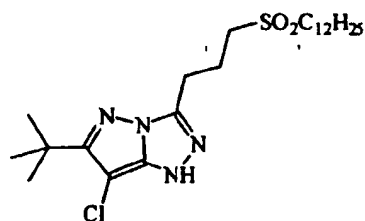


MAGENTA-2

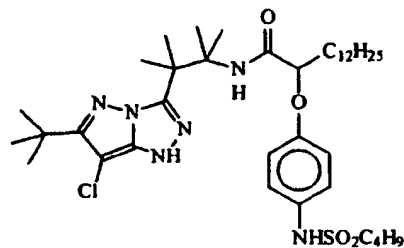
wherein R_a and R_b independently represent H or a substituent; R_c is a substituent (preferably an aryl group); R_d is a substituent (preferably an anilino, carbonamido, ureido, carbamoyl, alkoxy, aryloxy, carbonyl, alkoxy, aryloxy, carbonyl, or *N*-heterocyclic group); X is hydrogen or a coupling-off group; and Z_a , Z_b , and Z_c are independently a substituted methine group, $=N-$, $=C-$, or $-NH-$, provided that one of either the Z_a-Z_b bond or the Z_b-Z_c bond is a double bond and the other is a single bond, and when the Z_b-Z_c bond is a carbon-carbon double bond, it may form part of an aromatic ring, and at least one of Z_a , Z_b , and Z_c represents a methine group connected to the group R_b .

[0098] Specific examples of such couplers are:

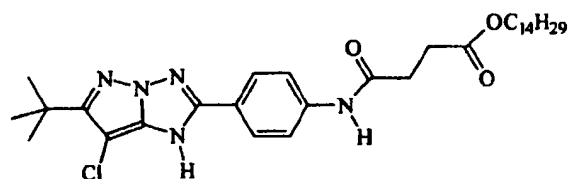
M-1



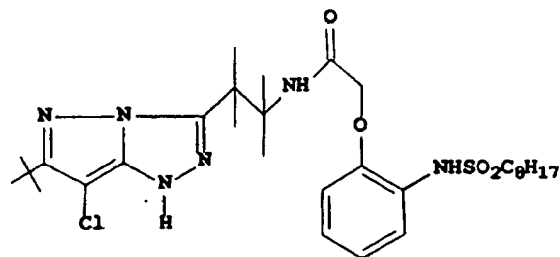
M-2



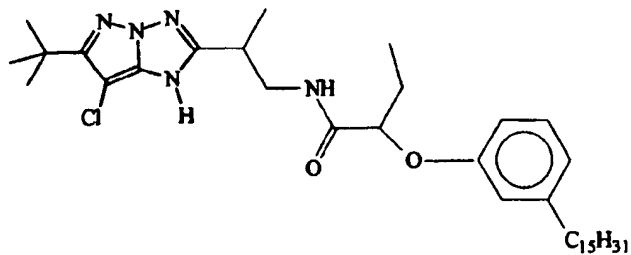
M-3



M-4



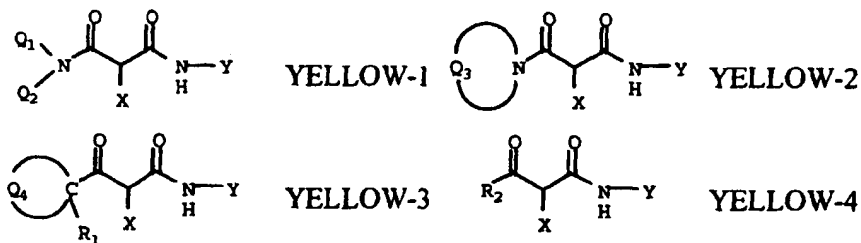
M-5



[0099] Couplers that form yellow dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Patent Nos. 2,298,443; 2,407,210; 2,875,057; 3,048,194; 3,265,506; 3,447,928; 3,960,570; 4,022,620; 4,443,536; 4,910,126; and 5,340,703 and "Farbkuppler-eine Literature Übersicht,"

published in Agfa Mitteilungen, Band III, pp. 112-126 (1961). Such couplers are typically open chain ketomethylene compounds. Also preferred are yellow couplers such as described in, for example, European Patent Application Nos. 482,552; 510,535; 524,540; 543,367; and U.S. Patent No. 5,238,803. For improved color reproduction, couplers which give yellow dyes that cut off sharply on the long wavelength side are particularly preferred (for example, see U.S. Patent No. 5,360,713).

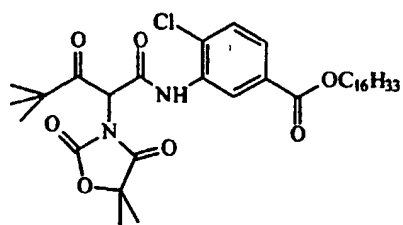
[0100] Typical preferred yellow couplers are represented by the following formulas:



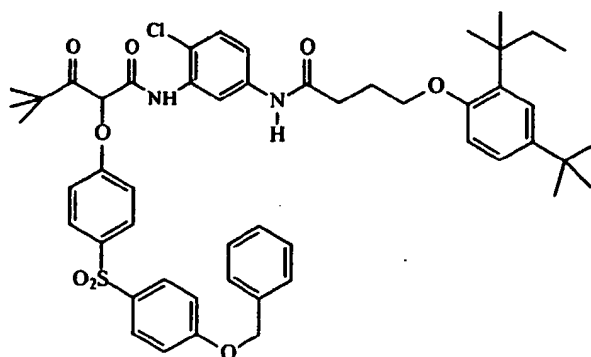
wherein R_1 , R_2 , Q_1 and Q_2 each represents a substituent; X is hydrogen or a coupling-off group; Y represents an aryl group or a heterocyclic group; Q_3 represents an organic residue required to form a nitrogen-containing heterocyclic group together with the $>N-$; and Q_4 represents nonmetallic atoms necessary to form a 3- to 5-membered hydrocarbon ring or a 3- to 5-membered heterocyclic ring which contains at least one hetero atom selected from N, O, S, and P in the ring. Particularly preferred is when Q_1 and Q_2 each represent an alkyl group, an aryl group, or a heterocyclic group, and R_2 represents an aryl or tertiary alkyl group.

[0101] Preferred yellow couplers can be of the following general structures

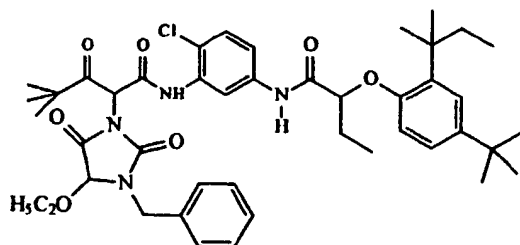
Y-1



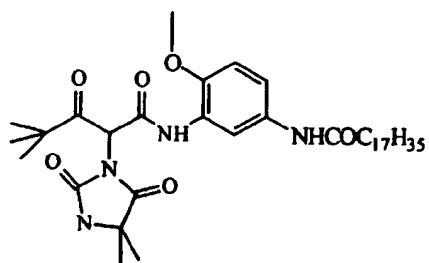
Y-2



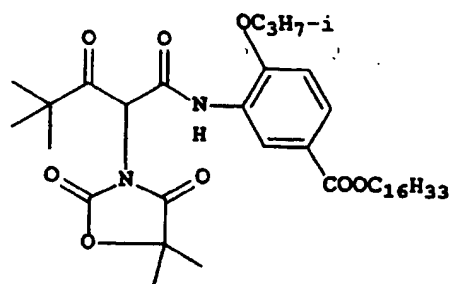
Y-3



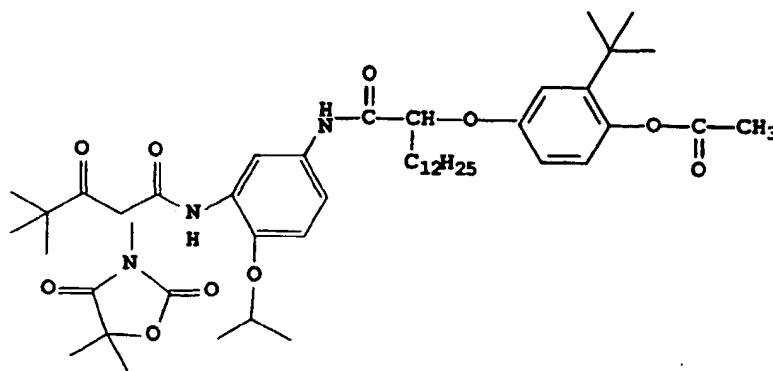
Y-4



Y-5



Y-6



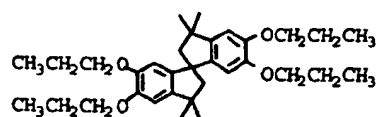
[0102] Unless otherwise specifically stated, substituent groups which may be substituted on molecules herein include any groups, whether substituted or unsubstituted, which do not destroy properties necessary for photographic utility. When the term "group" is applied to the identification of a substituent containing a substitutable hydrogen, it is intended to encompass not only the substituent's unsubstituted form, but also its form further substituted with any group or groups as herein mentioned. Suitably, the group may be halogen or may be bonded to the remainder of the molecule by an atom of carbon, silicon, oxygen, nitrogen, phosphorous, or sulfur. The substituent may be, for example, halogen, such as chlorine, bromine or fluorine; nitro; hydroxyl; cyano; carboxyl; or groups which may be further substituted, such as alkyl, including straight or branched chain alkyl, such as methyl, trifluoromethyl, ethyl, *t*-butyl, 3-(2,4-di-*t*-pentylphenoxy) propyl, and tetradecyl; alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, *sec*-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy, 2-(2,4-di-*t*-pentylphenoxy)ethoxy, and 2-dodecyloxyethoxy; aryl such as phenyl, 4-*t*-butylphenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthyloxy, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, alpha-(2,4-di-*t*-pentyl-phenoxy)acetamido, alpha-(2,4-di-*t*-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)-hexanamido, alpha-(4-hydroxy-3-*t*-butylphenoxy)-tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, N-methyltetradecanazido, N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and N-acetyl-N-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-*t*-butylphenoxy carbonylamino, phenylcarbonylamino, 2,5-(di-*t*-pentylphenyl)carbonylamino, *p*-dodecyl-phenylcarbonylamino, *p*-toluylcarbonylamino, N-methylureido, N,N-dimethylureido, N-methyl-N-dodecylureido, N-hexadecylureido, N,N-di-octadecylureido, N,N-di-octyl-N'-ethylureido, N-phenylureido, N,N-diphenylureido, N-phenyl-N-*p*-toluylureido, N-(*m*-hexadecylphenyl)ureido, N,N-(2,5-di-*t*-pentylphenyl)-N'-ethylureido, and *t*-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, *p*-toluylsulfonamido, *p*-dodecylbenzenesulfonamido, N-methyltetradecylsulfonamido, N,N-dipropyl-sulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-hexadecylsulfamoyl, N,N-dimethylsulfamoyl; N-[3-(dodecyloxy)propyl]sulfamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]sulfamoyl, N-methyl-N-tetradecylsulfamoyl, and N-dodecylsulfamoyl; carbamoyl, such as N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-octadecyl-

carbamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]carbamoyl, N-methyl-N-tetradecylcarbamoyl, and N,N-dioctylcarbamoyl; acyl, such as acetyl, (2,4-di-*t*-amylphenoxy)acetyl, phenoxycarbonyl, *p*-dodecyloxyphenoxycarbonyl, methoxycarbonyl, butoxycarbonyl, tetradecyloxy carbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxy carbonyl, and dodecyloxy carbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-*t*-pentylphenoxy sulfonyl, methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and *p*-toluylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and *p*-toluylsulfinyl; thio, such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-*t*-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-*t*-octylphenylthio, and *p*-tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, *p*-dodecylamidobenzoyloxy, N-phenylcarbamoxyloxy, N-ethylcarbamoxyloxy, and cyclohexylcarbamoxyloxy; amino, such as phenylanilino, 2-chloroanilino, diethylamino, dodecylamino; imino, such as 1 (N-phenylimido)ethyl, N-succinimido or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which may be substituted and which contain a 3 to 7 membered heterocyclic ring composed of carbon atoms and at least one hetero atom selected from the group consisting of oxygen, nitrogen and sulfur, such as 2-furyl, 2-thienyl, 2-benzimidazolyl or 2-benzothiazolyl; quaternary ammonium, such as triethylammonium; and silyloxy, such as trimethylsilyloxy.

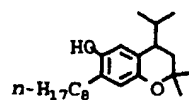
[0103] If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired photographic properties for a specific application and can include, for example, hydrophobic groups, solubilizing groups, blocking groups, releasing or releasable groups, etc. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

[0104] Representative substituents on ballast groups include alkyl, aryl, alkoxy, aryloxy, alkylthio, hydroxy, halogen, alkoxycarbonyl, aryloxycarbonyl, carboxy, acyl, acyloxy, amino, anilino, carbonamido, carbamoyl, alkylsulfonyl, arylsulfonyl, sulfonamido, and sulfamoyl groups wherein the substituents typically contain 1 to 42 carbon atoms. Such substituents can also be further substituted.

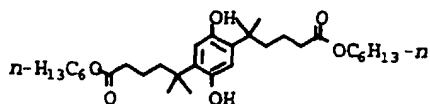
[0105] Stabilizers and scavengers that can be used in these photographic elements, but are not limited to, the following:



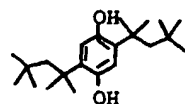
ST-1



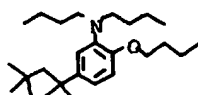
ST-2



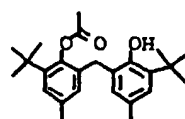
ST-3



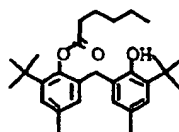
ST-4



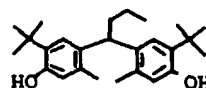
ST-5



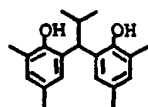
ST-6



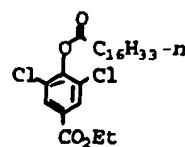
ST-7



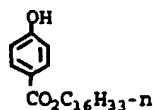
ST-8



ST-9



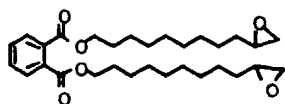
ST-10



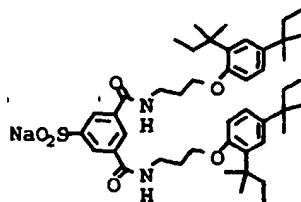
ST-11



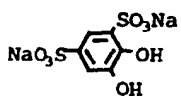
ST-12



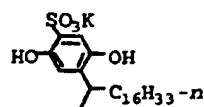
ST-13



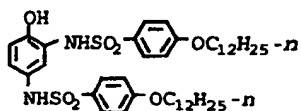
ST-14



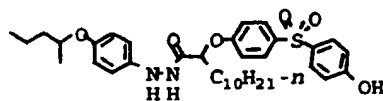
ST-15



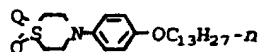
ST-16



ST-17



ST-18

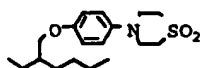


ST-19

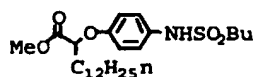


$n = 75-8,000$

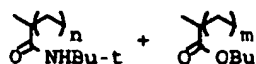
ST-20



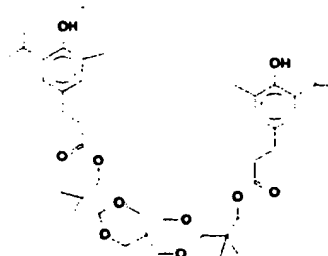
ST-21



ST-22



ST-23



ST-24

$n:m 1:1 \text{ mw} = 75-100,000$

Examples of solvents which may be used in the invention include the following:

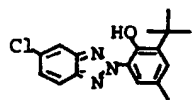
Tritolyl phosphate

S-1

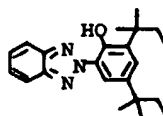
(continued)

Dibutyl phthalate	S-2
Diundecyl phthalate	S-3
<i>N,N</i> -Diethyldodecanamide	S-4
<i>N,N</i> -Dibutyldodecanamide	S-5
Tris(2-ethylhexyl)phosphate	S-6
Acetyl tributyl citrate	S-7
2,4-Di- <i>tert</i> -pentylphenol	S-8
2-(2-Butoxyethoxy)ethyl acetate	S-9
1,4-Cyclohexyldimethylene bis(2-ethylhexanoate)	S-10

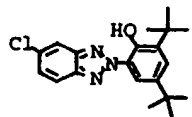
[0106] The dispersions used in photographic elements may also include ultraviolet (UV) stabilizers and so called liquid UV stabilizers such as described in U.S. Patent Nos. 4,992,358; 4,975,360; and 4,587,346. Examples of UV stabilizers are shown below.



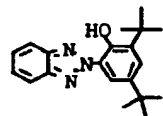
UV-1



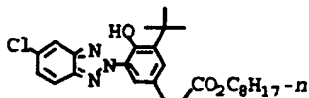
UV-2



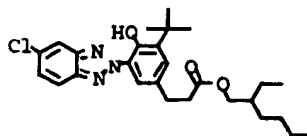
UV-3



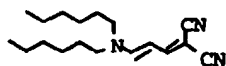
UV-4



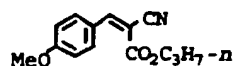
UV-5



UV-6

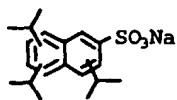


UV-7

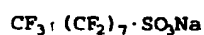


UV-8

[0107] The aqueous phase may include surfactants. Surfactant may be cationic, anionic, zwitterionic or non-ionic. Useful surfactants include, but are not limited to, the following:



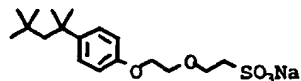
SF-1



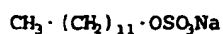
SF-2



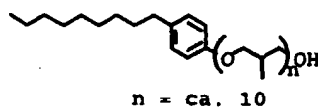
SF-3



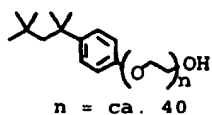
SF-4



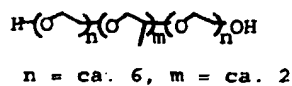
SF-5



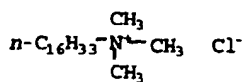
SF-6



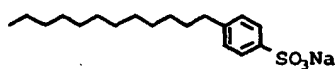
SF-7



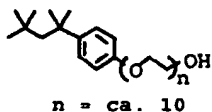
SF-8



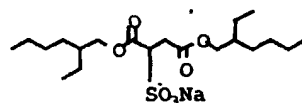
SF-9



SF-10



SF-11

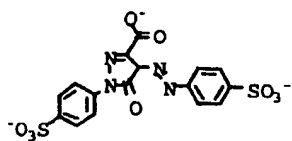


SF-12

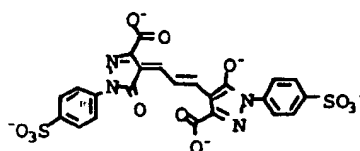
[0108] Further, it is contemplated to stabilize photographic dispersions prone to particle growth through the use of hydrophobic, photographically inert compounds such as disclosed by Zengerle et al in USSN 07/978,104.

[0109] The photographic elements may also contain filter dye layers comprising colloidal silver sol or yellow, cyan, and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Useful examples of absorbing materials are discussed in *Research Disclosure*, September 1996, Item 38957, Section VIII.

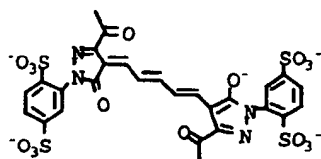
[0110] The photographic elements may also contain light absorbing materials that can increase sharpness and be used to control speed and minimum density. Examples of useful absorber dyes are described in U.S. 4,877,721; U.S. 5,001,043; U.S. 5,153,108; and U.S. 5,035,985. Solid particle dispersion dyes are described in U.S. Patent Nos. 4,803,150; 4,855,221; 4,857,446; 4,900,652; 4,900,653; 4,940,654; 4,948,717; 4,948,718; 4,950,586; 4,988,611; 4,994,356; 5,098,820; 5,213,956; 5,260,179; 5,266,454. Useful dyes include, but are not limited to, the following:



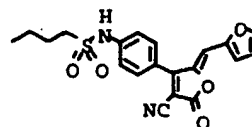
DYE-1



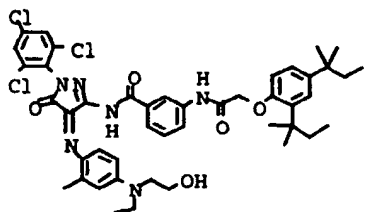
DYE-2



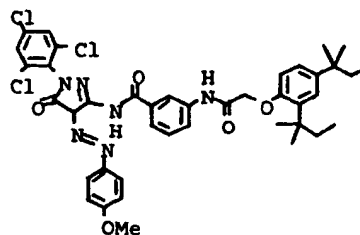
DYE-3



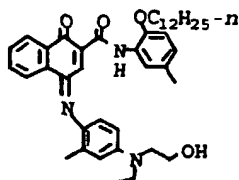
DYE-4



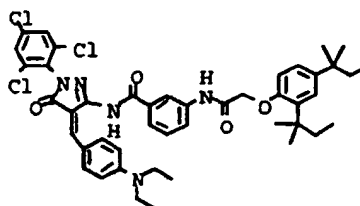
DYE-5



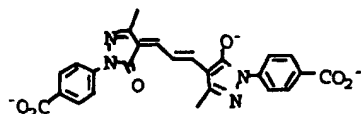
DYE-6



DYE-7



DYE-8



DYE-9

[0111] In a preferred embodiment the invention employs recording elements which are constructed to contain at least three silver halide emulsion layer units. A suitable full color, multilayer format for a recording element used in the invention is represented by Structure I.

5	Red-sensitized cyan dye image-forming silver halide emulsion unit
	Interlayer
10	Green-sensitized magenta dye image-forming silver halide emulsion unit
	Interlayer
15	Blue-sensitized yellow dye image-forming silver halide emulsion unit
20	//// Support ///

STRUCTURE I

wherein the red-sensitized, cyan dye image-forming silver halide emulsion unit is situated nearest the support; next in order is the green-sensitized, magenta dye image-forming unit, followed by the uppermost blue-sensitized, yellow dye image-forming unit. The image-forming units are separated from each other by hydrophilic colloid interlayers containing an oxidized developing agent scavenger to prevent color contamination. Silver halide emulsions satisfying the grain and gelatino-peptizer requirements described above can be present in any one or combination of the emulsion layer units. Additional useful multicolor, multilayer formats for an element of the invention include structures as described in U.S. Patent 5,783,373. Each of such structures in accordance with the invention preferably would contain at least three silver halide emulsions comprised of high chloride grains having at least 50 percent of their surface area bounded by {100} crystal faces and containing dopants from classes (i) and (ii), as described above. Preferably each of the emulsion layer units contains emulsion satisfying these criteria.

[0112] Conventional features that can be incorporated into multilayer (and particularly multicolor) recording elements contemplated for use in the method of the invention are illustrated by *Research Disclosure*, Item 38957, cited above:

XI. Layers and layer arrangements

XII. Features applicable only to color negative

XIII. Features applicable only to color positive

B. Color reversal

C. Color positives derived from color negatives

XIV. Scan facilitating features.

[0113] The recording elements comprising the radiation sensitive high chloride emulsion layers according to this invention can be conventionally optically printed, or in accordance with a particular embodiment of the invention can be image-wise exposed in a pixel-by-pixel mode using suitable high energy radiation sources typically employed in electronic printing methods. Suitable actinic forms of energy encompass the ultraviolet, visible and infrared regions of the electromagnetic spectrum as well as electron-beam radiation and is conveniently supplied by beams from one or more light emitting diodes or lasers, including gaseous or solid state lasers. Exposures can be monochromatic, orthochromatic or panchromatic. For example, when the recording element is a multilayer multicolor element, exposure can be provided by laser or light emitting diode beams of appropriate spectral radiation, for example, infrared, red, green or blue wavelengths, to which such element is sensitive. Multicolor elements can be employed which produce cyan, magenta and yellow dyes as a function of exposure in separate portions of the electromagnetic spectrum, including at least two portions of the infrared region, as disclosed in the previously mentioned U.S. Patent No. 4,619,892. Suitable exposures include those up to 2000 nm, preferably up to 1500 nm. Suitable light emitting diodes and commercially

available laser sources are known and commercially available. Imagewise exposures at ambient, elevated or reduced temperatures and/or pressures can be employed within the useful response range of the recording element determined by conventional sensitometric techniques, as illustrated by T.H. James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, Chapters 4, 6, 17, 18 and 23.

5 **[0114]** It has been observed that anionic $[MX_xY_yL_z]$ hexacoordination complexes, where M is a group 8 or 9 metal (preferably iron, ruthenium or iridium), X is halide or pseudohalide (preferably Cl, Br or CN) x is 3 to 5, Y is H_2O , y is 0 or 1, L is a C-C, H-C or C-N-H organic ligand, and Z is 1 or 2, are surprisingly effective in reducing high intensity reciprocity failure (HIRF), low intensity reciprocity failure (LIRF) and thermal sensitivity variance and in improving latent image keeping (LIK). As herein employed HIRF is a measure of the variance of photographic properties for equal exposures, but with exposure times ranging from 10^{-1} to 10^{-6} second. LIRF is a measure of the variance of photographic properties for equal exposures, but with exposure times ranging from 10^{-1} to 100 seconds. Although these advantages can be generally compatible with face centered cubic lattice grain structures, the most striking improvements have been observed in high (>50 mole %, preferably ≥ 90 mole %) chloride emulsions. Preferred C-C, H-C or C-N-H organic ligands are aromatic heterocycles of the type described in U.S. Pat. No. 5,462,849. The most effective C-C, H-C or C-N-H organic ligands are azoles and azines, either unsubstituted or containing alkyl, alkoxy or halide substituents, where the alkyl moieties contain from 1 to 8 carbon atoms. Particularly preferred azoles and azines include thiazoles, thiazolines and pyrazines.

[0115] The quantity or level of high energy actinic radiation provided to the recording medium by the exposure source is generally at least 10^{-4} ergs/cm², typically in the range of about 10^{-4} ergs/cm² to 10^{-3} ergs/cm² and often from 10^{-3} ergs/cm² to 10^2 ergs/cm². Exposure of the recording element in a pixel-by-pixel mode as known in the prior art persists for only a very short duration or time. Typical maximum exposure times are up to 100 μ seconds, often up to 10 μ seconds, and frequently up to only 0.5 μ seconds. Single or multiple exposures of each pixel are contemplated. The pixel density is subject to wide variation, as is obvious to those skilled in the art. The higher the pixel density, the sharper the images can be, but at the expense of equipment complexity. In general, pixel densities used in conventional electronic printing methods of the type described herein do not exceed 10^7 pixels/cm² and are typically in the range of about 10^4 to 10^6 pixels/cm². An assessment of the technology of high-quality, continuous-tone, color electronic printing using silver halide photographic paper which discusses various features and components of the system, including exposure source, exposure time, exposure level and pixel density and other recording element characteristics is provided in Firth et al., *A Continuous-Tone Laser Color Printer*, Journal of Imaging Technology, Vol. 14, No. 3, June 1988, which is hereby incorporated herein by reference. As previously indicated herein, a description of some of the details of conventional electronic printing methods comprising scanning a recording element with high energy beams such as light emitting diodes or laser beams, are set forth in Hioki U.S. patent 5,126,235, European Patent Applications 479 167 A1 and 502 508 A1.

[0116] Once imagewise exposed, the recording elements can be processed in any convenient conventional manner to obtain a viewable image. Such processing is illustrated by *Research Disclosure*, Item 38957, cited above:

XVIII. Chemical development systems

XIX. Development

XX. Desilvering, washing, rinsing and stabilizing

40 **[0117]** In addition, a useful developer for the inventive material is a homogeneous, single part developing agent. The homogeneous, single-part color developing concentrate is prepared using a critical sequence of steps:

[0118] In the first step, an aqueous solution of a suitable color developing agent is prepared. This color developing agent is generally in the form of a sulfate salt. Other components of the solution can include an antioxidant for the color developing agent, a suitable number of alkali metal ions (in an at least stoichiometric proportion to the sulfate ions) provided by an alkali metal base, and a photographically inactive water-miscible or water-soluble hydroxy-containing organic solvent. This solvent is present in the final concentrate at a concentration such that the weight ratio of water to the organic solvent is from about 15:85 to about 50:50.

[0119] In this environment, especially at high alkalinity, alkali metal ions and sulfate ions form a sulfate salt that is precipitated in the presence of the hydroxy-containing organic solvent. The precipitated sulfate salt can then be readily removed using any suitable liquid/solid phase separation technique (including filtration, centrifugation or decantation). If the antioxidant is a liquid organic compound, two phases may be formed and the precipitate may be removed by discarding the aqueous phase.

55 **[0120]** The color developing concentrates of this invention include one or more color developing agents that are well known in the art that, in oxidized form, will react with dye forming color couplers in the processed materials. Such color developing agents include, but are not limited to, aminophenols, *p*-phenylenediamines (especially *N,N*-dialkyl-*p*-phenylenediamines) and others which are well known in the art, such as EP 0 434 097A1 (published June 26, 1991) and EP 0 530 921A1 (published March 10, 1993). It may be useful for the color developing agents to have one or more

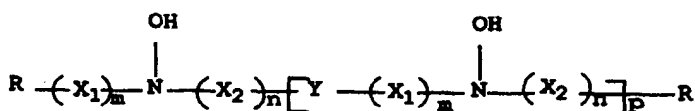
water-solubilizing groups as are known in the art. Further details of such materials are provided in *Research Disclosure*, publication 38957, pages 592-639 (September 1996). *Research Disclosure* is a publication of Kenneth Mason Publications Ltd., Dudley House, 12 North Street, Emsworth, Hampshire PO10 7DQ England (also available from Emsworth Design Inc., 121 West 19th Street, New York, N.Y. 10011). This reference will be referred to hereinafter as "*Research Disclosure*".

[0121] Preferred color developing agents include, but are not limited to, N,N-diethyl *p*-phenylenediamine sulfate (KODAK Color Developing Agent CD-2), 4-amino-3-methyl-N-(2-methanesulfonamidoethyl)aniline sulfate, 4-(N-ethyl-N- β -hydroxyethylamino)-2-methylaniline sulfate (KODAK Color Developing Agent CD-4), *p*-hydroxyethylethylaminoaniline sulfate, 4-(N-ethyl-N-2-methanesulfonamidoethyl)-2-methylphenylenediamine sesquisulfate (KODAK Color Developing Agent CD-3), 4-(N-ethyl-N-2-methanesulfonamidoethyl)-2-methylphenylenediamine sesquisulfate, and others readily apparent to one skilled in the art.

[0122] In order to protect the color developing agents from oxidation, one or more antioxidants are generally included in the color developing compositions. Either inorganic or organic antioxidants can be used. Many classes of useful antioxidants are known, including but not limited to, sulfites (such as sodium sulfite, potassium sulfite, sodium bisulfite and potassium metabisulfite), hydroxylamine (and derivatives thereof), hydrazines, hydrazides, amino acids, ascorbic acid (and derivatives thereof), hydroxamic acids, aminoketones, mono- and polysaccharides, mono- and polyamines, quaternary ammonium salts, nitroso radicals, alcohols, and oximes. Also useful as antioxidants are 1,4-cyclohexadienes. Mixtures of compounds from the same or different classes of antioxidants can also be used if desired.

[0123] Especially useful antioxidants are hydroxylamine derivatives as described for example, in U.S. Patents 4,892,804; 4,876,174; 5,354,646, and 5,660,974, all noted above, and US 5,646,327 (Burns et al). Many of these antioxidants are mono- and dialkylhydroxylamines having one or more substituents on one or both alkyl groups. Particularly useful alkyl substituents include sulfo, carboxy, amino, sulfonamido, carbonamido, hydroxy and other solubilizing substituents.

[0124] More preferably, the noted hydroxylamine derivatives can be mono- or dialkylhydroxylamines having one or more hydroxy substituents on the one or more alkyl groups. Representative compounds of this type are described, for example, in US-A-5,709,982 (Marrese et al), incorporated herein by reference, as having the structure I:



wherein R is hydrogen, a substituted or unsubstituted alkyl group of 1 to 10 carbon atoms, a substituted or unsubstituted hydroxyalkyl group of 1 to 10 carbon atoms, a substituted or unsubstituted cycloalkyl group of 5 to 10 carbon atoms, or a substituted or unsubstituted aryl group having 6 to 10 carbon atoms in the aromatic nucleus.

[0125] X_1 is $-CH_2(OH)CH(R_1)-$ and X_2 is $-CH(R_1)CH_2(OH)-$ wherein R_1 and R_2 are independently hydrogen, hydroxy, a substituted or unsubstituted alkyl group of 1 or 2 carbon atoms, a substituted or unsubstituted hydroxyalkyl group of 1 or 2 carbon atoms, or R_1 and R_2 together represent the carbon atoms necessary to complete a substituted or unsubstituted 5- to 8-membered saturated or unsaturated carbocyclic ring structure.

[0126] Y is a substituted or unsubstituted alkylene group having at least 4 carbon atoms, and has an even number of carbon atoms, or Y is a substituted or unsubstituted divalent aliphatic group having an even total number of carbon and oxygen atoms in the chain, provided that the aliphatic group has at least 4 atoms in the chain.

[0127] Also in Structure I, m, n and p are independently 0 or 1. Preferably, each of m and n is 1, and p is 0.

[0128] Specific di-substituted hydroxylamine antioxidants include, but are not limited to: N,N-bis(2,3-dihydroxypropyl)hydroxylamine, N,N-bis(2-methyl-2,3-dihydroxypropyl)hydroxylamine and N,N-bis(1-hydroxymethyl-2-hydroxy-3-phenylpropyl)hydroxylamine. The first compound is preferred.

[0129] The following examples illustrate the practice of this invention. They are not intended to be exhaustive of all possible variations of the invention. Parts and percentages are by weight unless otherwise indicated.

EXAMPLES

Example 1

[0130] In this example the color silver halide emulsion of the invention was coated on a typical polyethylene melt extrusion coated cellulose paper base (Kodak Ektacolor™ Edge 7). The invention was compared to a control color paper which is a typical consumer color paper. This example will show the color silver halide emulsion of the invention can be exposed in a digital printing process as well as a negative working optical printing process where as the control

paper is limited to a negative working optical printing process only.

Photographic grade cellulose paper used in the invention and control:

5 [0131] A photographic paper support was produced by refining a pulp furnish of 100% bleached hardwood Kraft
trough a double disk refiner, then a Jordan conical refiner. To the resulting pulp furnish was added 0.8% sodium stear-
ate, 0.5% aluminum chloride, 0.15% stilbene triazine FWA, 0.2% polyamideepichlorohydrin, 0.7% anionic polyacryla-
mide, and 0.6% TiO_2 on a dry weight basis. An about 31.5 lbs. per 1000 sq. ft. (ksf) bone dry weight base paper was
10 made on a fourdrinier paper machine, wet pressed to a solid of 42%, and dried to a moisture of 3% using steam-heated
dryers achieving an apparent density of 0.70 g/cc. The paper base was then surface sized using a vertical size press
with a 16% hydroxyethylated cornstarch solution to achieve a loading of 4.2 wt.% starch. The surface sized support was
dried to a moisture of 8.8% using steam-heated dryers and calendered to an apparent density of 1.08 gm/cc.

[0132] A resin concentrate was formed for the invention and the control using a continuous mixer 43.5% of an ana-
tase TiO_2 , 1% Zinc stearate, 0.15% optical brightener, 0.3% of the hindered amine poly[[6-[(1,1,3,3-tetramethyl-
15 butyl)amino]-s-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidyl)imino]hexamethylene[(2,2,6,6-tetramethyl-4-
piperidyl)imino]] with a molecular weight of greater than 2500, 0.6% blue colorant, and 0.002% red colorant were
blended to make a concentrated pellet. 33% of each of the above resins from were blended with 67% low-density pol-
yethylene and 25 μm of the resin blend was extrusion coated onto the photographic cellulose paper. The resins were
20 extruded at 800ft/min using an Eagan 2.5" extruder. The temperature of the extruded polymer was varied from at 560°F
to 600°F.

[0133] Silver chloride emulsions were chemically and spectrally sensitized as described below. A biocide compris-
ing a mixture of N-methyl-isothiazolone and N-methyl-5-chloro-isthiazolone was added after sensitization.

25 **Blue Sensitive Emulsion (Blue EM-1).** A high chloride silver halide emulsion is precipitated by adding approxi-
mately equimolar silver nitrate and sodium chloride solutions into a well stirred reactor containing glutaryl diami-
nophenyldisulfide, gelatin peptizer and thioether ripener. Cesium pentachloronitrosylsulfate(II) dopant is added
during the silver halide grain formation for most of the precipitation, followed by the addition of potassium hexacy-
anoruthenate(II), potassium (5-methylthiazole)-pentachloroiridate, a small amount of KI solution, and shelling with-
out any dopant. The resultant emulsion contains cubic shaped grains having edge length of 0.6 μm . The emulsion
30 is optimally sensitized by the addition of a colloidal suspension of aurous sulfide and heat ramped to 60°C during
which time blue sensitizing dye BSD-4, potassium hexachloroiridate, Lippmann bromide and 1-(3-acetamidophe-
nyl)-5-mercaptotetrazole were added.

35 **Green Sensitive Emulsion (Green EM-1):** A high chloride silver halide emulsion is precipitated by adding approx-
imately equimolar silver nitrate and sodium chloride solutions into a well stirred reactor containing, gelatin peptizer
and thioether ripener. Cesium pentachloronitrosylsulfate(II) dopant is added during the silver halide grain forma-
tion for most of the precipitation, followed by the addition of potassium (5-methylthiazole)-pentachloroiridate. The
resultant emulsion contains cubic shaped grains of 0.3 μm in edgelenlength size. The emulsion is optimally sensitized
40 by the addition of glutaryl diaminophenyldisulfide, a colloidal suspension of aurous sulfide and heat ramped to 55°C
during which time potassium hexachloroiridate doped Lippmann bromide, a liquid crystalline suspension of green
sensitizing dye GSD-1, and 1-(3-acetamidophenyl)-5-mercaptotetrazole were added.

45 **Red Sensitive Emulsion (Red EM-1):** A high chloride silver halide emulsion is precipitated by adding approxi-
mately equimolar silver nitrate and sodium chloride solutions into a well stirred reactor containing gelatin peptizer
and thioether ripener. During the silver halide grain formation, potassium hexacyanoruthenate(II) and potassium (5-
methylthiazole)-pentachloroiridate are added. The resultant emulsion contains cubic shaped grains of 0.4 μm in
edgelenlength size. The emulsion is optimally sensitized by the addition of glutaryl diaminophenyldisulfide, sodium thi-
osulfate, tripotassium bis {2-[3-(2-sulfobenzamido)phenyl]-mercaptotetrazole} gold(I) and heat ramped to 64°C
50 during which time 1-(3-acetamidophenyl)-5-mercaptotetrazole, potassium hexachloroiridate, and potassium bro-
mide are added. The emulsion is then cooled to 40°C, pH adjusted to 6.0 and red sensitizing dye RSD-1 is added.

[0134] Coupler dispersions were emulsified by methods well known to the art and the following layers were coated
on the following support:

55 [0135] The following light sensitive silver halide imaging layers were utilized to prepare photographic print materials
for the invention. The following imaging layers were coated utilizing curtain coating.

Layer	Item	Laydown (g/m ²)
Layer 1	Blue Sensitive Layer	
	Gelatin	1.3127
	Blue sensitive silver (Blue EM-1)	0.2399
	Y-4	0.4143
	ST-23	0.4842
	Tributyl Citrate	0.2179
	ST-24	0.1211
	ST-16	0.0095
	Sodium Phenylmercaptotetrazole	0.0001
	Piperidino hexose reductone	0.0024
	5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1)	0.0002
	SF-1	0.0366
	Potassium chloride	0.0204
	Dye-1	0.0148
Layer 2	Interlayer	
	Gelatin	0.7532
	ST-4	0.1076
	S-3	0.1969
	5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1)	0.0001
	Catechol disulfonate	0.0323
	SF-1	0.0081

Layer 3	Green Sensitive Layer	
	Gelatin	1.1944
	Green Sensitive Silver (Green EM-1)	0.1011
	M-4	0.2077
	Oleyl Alcohol	0.2174
	S-3	0.1119
	ST-21	0.0398
	ST-22	0.2841
	Dye-2	0.0073
	5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1)	0.0001
	SF-1	0.0236
	Potassium chloride	0.0204
	Sodium Phenylmercaptotetrazole	0.0007
Layer 4	M/C Interlayer	
	Gelatin	0.7532
	ST-4	0.1076
	S-3	0.1969
	Acrylamide/t-Butylacrylamide sulfonate copolymer	0.0541
	Bis-vinylsulfonylmethane	0.1390
	3,5-Dinitrobenzoic acid	0.0001
	Citric acid	0.0007
	Catechol disulfonate	0.0323
	5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1)	0.0001
Layer 5	Red Sensitive Layer	
	Gelatin	1.3558
	Red Sensitive silver (Red EM-1)	0.1883
	IC-35	0.2324
	IC-36	0.0258
	UV-2	0.3551
	Dibutyl sebacate	0.4358
	S-6	0.1453
	Dye-3	0.0229
	Potassium p-toluenethiosulfonate	0.0026
	5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1)	0.0001
	Sodium Phenylmercaptotetrazole	0.0005
	SF-1	0.0524

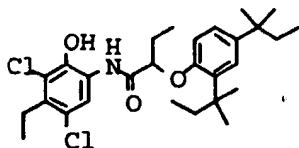
5	Layer 6	UV Overcoat	
		Gelatin	0.8231
		UV-1	0.0355
		UV-2	0.2034
		ST-4	0.0655
10		SF-1	0.0125
		S-6	0.0797
		5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1)	0.0001
15	Layer 7	SOC	
		Gelatin	0.6456
		Ludox AM™ (colloidal silica)	0.1614
		Polydimethylsiloxane (DC200™)	0.0202
20		5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1)	0.0001
		SF-2	0.0032
		Tergitol 15-S-5™ (surfactant)	0.0020
25		SF-1	0.0081
		Aerosol OT™ (surfactant)	0.0029

[0136] Coating format 1 was utilized to prepare the photographic print materials for the control. The control silver layers did not have the (i) and (ii) dopants and generally correspond to commercially available emulsions. None of the silver layers has (ii). The following imaging layers were coated utilizing curtain coating.

	Coating Format 1	Laydown mg/m²
35	Layer 1	Blue Sensitive Layer
		Gelatin 1300
40		Blue sensitive silver 200
		Y-1 440
		ST-23 440
45		S-2 190
	Layer 2	Interlayer
		Gelatin 650
		ST-4 55
50		S-2 160

	Layer 3	Green Sensitive	
5		Gelatin	1100
		Green sensitive silver	70
		M-1	270
		S-2	75
10		S-3	32
		ST-8	20
		ST-21	165
		ST-22	530
15	Layer 4	UV Interlayer	
		Gelatin	635
		UV-1	30
		UV-2	160
20		ST-4	50
		S-10	30
		S-2	30
25	Layer 5	Red Sensitive Layer	
		Gelatin	1200
		Red sensitive silver	170
		C-1	365
30		S-2	360
		UV-2	235
		S-9	30
		ST-4	3
35	Layer 6	UV Overcoat	
		Gelatin	440
		UV-1	20
40		UV-2	110
		ST-4	30
		S-10	20
		S-2	20
45	Layer 7	SOC	
		Gelatin	490
		ST-4	17
		SiO ₂	200
50		Surfactant	2

55



C-1

[0137] The D LogH characteristic curves were generated for the invention and control materials by electromodulated separation exposures (raster scanned) at 1000 nanoseconds. The 0.5 second exposures were made by contact printing using a carbon step tablet and separation filters. The 1000 ns digital exposures and the 0.5 second contact printed exposures were processed in conventional RA4 development chemistry and read on a Status A reflection densitometer. The separation curves were plotted and shoulder density maximum and inmax values were taken from the plots. Figure 1 shows a D LogH characteristic curve. The Dmin value 10 is the intercept of the curve on the density axis, 12 is Dmax (maximum density), 14 is the speed point, 16 is the shoulder and 18 is the inmax value. The distance between 10 and .04 units higher than 10 is indicated at 22. A % loss value was calculated for the shoulder, density maximum and inmax. The % loss equation used was % loss = ((0.5 sec exposure value-1000 ns exposure value)/0.5 sec exposure value) * 100. The % loss values from the D LogH characteristic curves are listed in Table 1 below.

TABLE 1

	Check	Feature
	% loss (0.5 secs vs 1000 ns)	% loss (0.5 sec vs 1000 ns)
Red Shoulder	-37.3	-7.0
Green Shoulder	-19.6	-5.4
Blue Shoulder	-27.8	-2.3
Red Dmax	-29.9	-3.4
Green Dmax	-19.6	-6.4
Blue Dmax	-16.9	-2.5
Red inmax	-42.7	-6.7
Green inmax	-23.3	-7.3
Blue inmax	-33.1	-2.6

[0138] The data from Table 1 clearly demonstrate the digital printing advantages that the invention has compared to the control. Since an ideal color paper would have a theoretical % loss of zero across this extreme exposure range, a % loss of less than 10% in all color records is considered exceptional. For shoulder, Dmax and inmax, the invention is clearly superior to the control color paper and is attributed to the significant and unexpected reciprocity control enabled by the formulation of the invention. Because the color paper of the invention can be exposed over this extreme range of exposures (0.5 seconds to 1000 ns) with a % loss of less than 10% for each color record, the color paper of the invention has significant commercial value in that it can function in both a negative working optical exposure equipment and direct writing sub microsecond digital systems.

Claims

1. A negative working reflective base photographic element comprising support material wherein said support material comprises a paper base and overlaying said paper base are full color photographic silver halide containing imaging layers wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 10 percent as a function of the red shoulder color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 8 percent as a function of the green shoulder color record, wherein said pho-

tographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 5 percent as a function of the blue shoulder color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 6 percent as a function of the red Dmax color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 9 percent as a function of the green Dmax color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 5 percent as a function of the blue Dmax color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 9 percent as a function of the red inmax color record, wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 10 percent as a function of the green inmax color record, and wherein said photographic element has an exposure range of between 1000 nanoseconds and 0.5 seconds when there is a density loss of no more than 5 percent as a function of the blue inmax color record.

2. The element of Claim 1 wherein when said element is digitally exposed at sub microsecond times of exposure at a maximum density of 2.2 and then developed it has substantially no fringing.
3. The element of Claim 1 wherein the silver halide grains of the full color photographic element are comprised of at least 90 percent silver chloride and further comprise an iridium coordination complex containing a thiazole or substituted thiazole ligand.
4. The element of Claim 3 further comprising a hexacoordination metal complex which satisfies the formula:



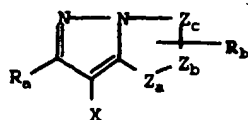
wherein

n is zero, -1, -2, -3 or -4;

M is a filled frontier orbital polyvalent metal ion, other than iridium; and

L_6 represents bridging ligands which can be independently selected, provided that at least four of the ligands are anionic ligands, and at least one of the ligands is a cyano ligand or a ligand more electronegative than a cyano ligand.

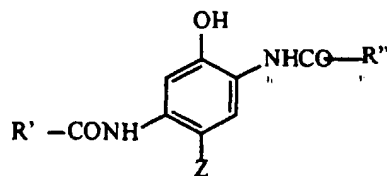
5. The element of Claim 1 wherein said element comprises



wherein

R_a and R_b independently represents H or a substituent; X is hydrogen or a coupling-off group; and Z_a , Z_b and Z_c are independently a substituted methine group, $=N-$, $=C-$, or $-NH-$, provided that one of either the Z_a-Z_b bond or the Z_b-Z_c bond is a double bond and the other is a single bond, and when the Z_b-Z_c bond is a carbon-carbon double bond, it may form part of an aromatic ring, and at least one of Z_a , Z_b , and Z_c represents a methine group connected to the group R_b .

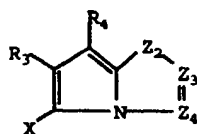
6. The element of Claim 1 wherein said element comprises



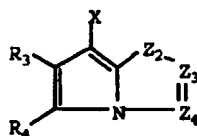
wherein

R' and R" are substituents selected such that the coupler is a "NB coupler", as herein defined; and Z is a hydrogen atom or a group which can be split off by the reaction of the coupler with an oxidized color developing agent.

or

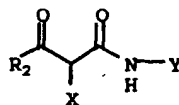


wherein R₃ and R₄ each represents an electron attractive group having a Hammett's substituent constant σ_{para} of 0.2 or more and the sum of the σ_{para} values of R₃ and R₄ is 0.65 or more, Z₂ represents —C(R₇)= and —N=; Z₃ and Z₄ each represents —C(R₈)= and —N=;



or wherein R₃ and R₄ each represents an electron attractive group having a Hammett's substituent constant σ_{para} of 0.2 or more and the sum of the σ_{para} values of R₃ and R₄ is 0.65 or more, Z₂ represents —C(R₇)= and —N=; Z₃ and Z₄ each represents —C(R₈)= and —N=.

7. The element of Claim 1 wherein said element comprises

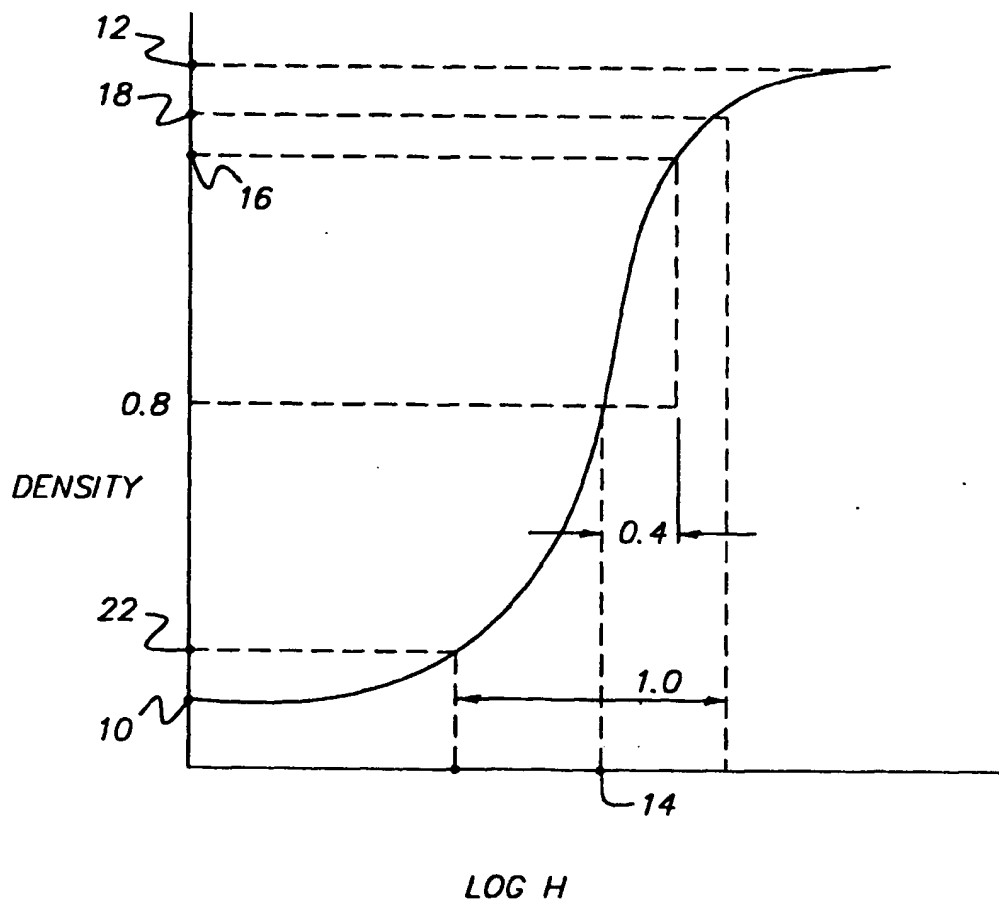


wherein X is hydrogen or a coupling-off group; Y represents an aryl group or a heterocyclic group; and R₂ is a substituent.

8. The support material of Claim 1 wherein the support comprises a paper substrate and at least one layer adjacent said paper comprising polyolefin polymer and a hindered amine stabilizer wherein said hindered amine stabilizer has a number average molecular weight of less than 2300.

9. The support material of Claim 1 further comprising a phenol antioxidant.

10. The support material of Claim 1 further comprising a phosphite antioxidant.





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 20 1365

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 728 516 A (CHEN BENJAMIN TEH-KUNG ET AL) 17 March 1998 (1998-03-17) * column 72, emulsion KK * * claims 1,10-12; example XXIII * * column 74, line 51 - line 58 *	1-10	G03C7/30 G03C1/09
D,X	US 5 783 373 A (BELL ERIC L ET AL) 21 July 1998 (1998-07-21) * column 13, line 45 - column 14, line 46; claims 1,13-19 *	1-10	
D,X	US 5 474 888 A (BELL ERIC L) 12 December 1995 (1995-12-12) * column 8, line 1 - line 5; claims 1-25 *	1-10	
D,A	US 5 457 021 A (OLM MYRA T ET AL) 10 October 1995 (1995-10-10) * claims 1,3,23 *	1-10	
D,A	EP 0 774 689 A (EASTMAN KODAK CO) 21 May 1997 (1997-05-21) * page 28, line 34 - page 32, line 7 *	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 7 August 2000	Examiner Bolger, W
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1603 03.82 (P4/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 20 1365

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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07-08-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5728516 A	17-03-1998	EP 0718676 A JP 8234340 A	26-06-1996 13-09-1996
US 5783373 A	21-07-1998	NONE	
US 5474888 A	12-12-1995	JP 8211529 A	20-08-1996
US 5457021 A	10-10-1995	NONE	
EP 0774689 A	21-05-1997	US 5744287 A JP 9171237 A	28-04-1998 30-06-1997

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82